THE ANALYSIS OF RUBBER

BY

JOHN B. TUTTLE

AGRICULTURAL COLL
No.
10 JUN 1924
COIMBATORE

American Chemical Society
Monograph Series

BOOK DEPARTMENT

The CHEMICAL CATALOG COMPANY, *Inc.*

19 EAST 24TH STREET, NEW YORK, U. S. A.

1922

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Press of
J. J. Little & Ives Company
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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

The development of knowledge in all branches of science, and

especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coördinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is

a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of coöperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

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PREFACE

The tendency of the industry is towards simplification of methods and materials. The readjustment of conditions to the basis of an adequate supply of crude rubber—a condition which did not obtain twenty years ago—has by the operation of natural economic laws eliminated from general use many pigments, rubber substitutes, and low grades of rubber. These are not likely to return, and we may dismiss them from consideration, confining ourselves to the materials found in the every day life of the industry as it exists today.

In any work on analysis, and especially on industrial substances, it is impossible to avoid the presentation of the subject from a very personal point of view. Many methods, and modifications of methods, are written on a single phase of the analysis, with a great variety of purposes back of them. In the analysis of rubber, methods have been published because they were shorter than existing ones; some used less expensive materials, or more simple equipment; and some because they really were an improvement. Few of these methods were thoroughly developed before publication; the user must discover for himself the limits of error and applicability. It is usually safer to hold fast to such methods as have stood the test of time, and whenever there may be any methods for any part of a rubber analysis which are not included herewith, it is because data are lacking as to their ability to accomplish the desired purpose. The omission does not imply lack of merit, but merely that sufficient experimental evidence is not yet forthcoming to warrant an unqualified approval.

Primarily, this monograph is addressed to the chemists in the consumers' laboratories, and to those who, without any previous experience in the technology or analysis of rubber, may be called upon to deal with a problem in which the composition of rubber may play a more or less important part. Nevertheless, it is the author's hope that it may not come amiss to those colleagues comprizing the technical staff of the laboratories of the manufacturing plants, who may find it desirable to study a competi-

tor's product, or who may be required to produce materials to accord with the consumers' specifications.

In view of the probability of this monograph reaching chemists of limited experience in the technology of rubber, Appendix A, on the methods of preparation of rubber compounds, and Appendix B, on the physical testing of rubber, have been added. These appendices are necessarily elemental in character, but they may serve as connecting links between these subjects, and the chemistry of the analysis of rubber.

J. B. T.

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COIMBATORE

THE ANALYSIS OF RUBBER

Chapter I.

The Purpose of Rubber Analysis.

The growth of the rubber industry has been tremendous, especially, so far as volume is concerned, since the advent of the pneumatic tire. More than any one other cause, the resiliency afforded by the pneumatic bicycle tire was responsible for the wide spread popularity of the bicycle, and the rubber automobile tire has played an equally, if not more important rôle in the development of motor driven vehicles. In the production of the various rubber articles, besides the essential rubber and sulfur which make up the vulcanized rubber, we need a vast volume of pigments or fillers, because by their use we may modify the properties of the vulcanized rubber so as to attain a degree of service which would otherwise be impossible. We must not, therefore, look upon these added substances as adulterants, or even mere diluents, but as integral parts of the whole, for by their service they have earned the right to due consideration. Some, it is true, are largely valuable, owing to the fact that they lower the cost of the products in which they are included. The rubber industry makes big demands upon the producers of raw materials, such as zinc oxide and sulfide, lead compounds, carbon black, magnesium oxide, and talc, and were we forced to depend upon these pigments alone, the costs would soon rise to prohibitive heights, with concomitant injury not merely to the rubber industry, but to others as well, such as paints and inks, which depend for their existence upon an adequate supply of these same pigments. We are thus doubly obliged to seek far and wide for new materials which will accomplish one of two things: produce the same or even better quality at a lower cost, or a better quality at the same cost.

In every line, there is a more or less clearly defined standard

of service, and the future of the industry is quite definitely tied up with the results obtained in the present by the attainment of that standard. In order to use correctly any material, it is important that we know the degree of purity of the commercial grades, the influence of possible impurities upon the quality of the products, and, most important of all, the degree of uniformity obtainable from one period to another. These data can be secured only through careful and persistent testing of the raw and finished materials.

It is not our purpose here to undertake a description of the functions and usage of the various materials to be mentioned later, but merely to discuss them from the point of view of their chemical properties. For the various other phases of the subject, the reader is referred to the bibliography which is included herewith.

What Is "Rubber"?

Probably few words in general usage are applied as generally as the word rubber. Strictly speaking, the word belongs to the polyterpene having the formula $(C_{10}H_{16})_x$. We know, however, that there is an homologous series of these polymerized products differing from each other by the constant quantity 2 CH_2, and these products have so many of the qualities peculiar to $(C_{10}H_{16})_x$ that they too are called rubber. Thus we may say that there is a rubber series analagous to the paraffin series, etc. The planters who cultivate the plantations call their product rubber, or crude rubber, although, in addition to the polyterpene, there is 2% and upwards of acetone-soluble substances called resins; 2 to 6% of nitrogenous substances, akin to the proteins; and small amounts of substances possessing the properties of catalysts of the vulcanization process. The manufacturer produces rubber products, although in addition to the rubber as obtained from the plantations, many other substances are added, both organic and inorganic, because of certain qualities which such additions produce in the finished article. Moreover, chemically speaking, we have in the hot vulcanized articles an entirely new series of products, viz., the sulfur addition products of the polyterpene, a series which passes from the extreme of pure rubber at one end to a constant composition of $(C_{10}H_{16}S_2)_x$ at the other end.

In order to avoid confusion, for our own purposes we will use the term "rubber" to mean any mixture of $(C_{10}H_{16})_x$ (its homologues are negligible commercially, at present) with any other substances, in either the vulcanized or unvulcanized state. "Crude rubber" will apply only to the materials as obtained from the rubber trees; and where the polyterpene itself is indicated, we will use the term "rubber hydrocarbon." "Rubber compound" will be used to indicate the formula of a commercial mixing.

From an analytical point of view, it is of little consequence whether the unit in the molecule of rubber is C_5H_8 or $C_{10}H_{16}$. There seems to be a preponderance of evidence in favor of the latter; in any event, we do know that while rubber can be synthesized from isoprene, $CH_2{:}C(CH_3).CH{:}CH_2$, the rubber molecule itself contains only one double bond for each group of C_5H_8. By vulcanizing rubber with a large excess of sulfur, C. O. Weber obtained a hard rubber corresponding to $C_{10}H_{16}S_2)_x$. With bromine, rubber has been found to form $(C_{10}H_{16}Br_4)_x$. These experiments have been repeated so many times, that there seems to be no necessity for further argument as to the existence of the two double bonds. The importance of this fact is seen when we realize that this fact is the basis upon which have been built the two classes of direct determinations of rubber, the tetrabromide, and the nitrosite, both of which will be discussed in their proper place.

The Need for Chemical Analysis of Rubber.

Any scheme which may be suggested for the analysis of rubber, either vulcanized or unvulcanized, must take into consideration the fact that there are two groups, with widely differing points of view, which are interested in the subject. We have first the manufacturers' chemists, who test their own products to determine what changes have taken place during the process of manufacture; and their competitors, products to ascertain what the latter are using. Analysts of this group may use methods which their knowledge of the subject tells them will give accurate results, even though it is known that such methods are not universally applicable. The second group embraces the consumers, who, as a rule, are endeavoring to learn whether or not the article complies with certain stipulated requirements, or specifications,

Here a definite procedure is obligatory, for in order to avoid disputes, the specifications usually (and if they do not, they should),[1] contain a more or less detailed description of the analytical methods. Since the composition is unknown, it is clear that the methods in use by the consumers should be as nearly universally applicable as it is possible to make them. From time to time, there have appeared suggestions for making analyses of rubber compounds, but too frequently the authors have neglected to take into consideration these different points of view, and this omission has materially reduced the value of the suggestions.

Rubber is a hydrocarbon of the terpene family, existing in a polymerized form, and having the composition $(C_{10}H_{16})_x$. The size of the molecule is unknown, although it is believed to be quite large, but we do know that each group of $C_{10}H_{16}$ contains two double bonds. Double bonds are unstable, and there is always a tendency for such double bonds to add various elements, or group of elements, which will tend to produce a more stable form. Thus we find that the double bonds of rubber may take up oxygen, ozone, sulfur, selenium, sulfur chloride, chlorine, bromine, etc., producing new chemical substances with distinctly new properties, many of which are more useful in a commercial sense than the original substance. Industrially, the most important of these compounds are those formed by the addition of sulfur, and sulfur monochloride, the chemical process being termed "vulcanization," or "curing." Crude rubber is a soft, plastic substance, soluble in naphtha, benzene, chloroform, carbon bisulfide, from which, by the simple process of evaporation, it may be recovered in its original form. The addition of comparatively small amounts of sulfur is sufficient to destroy the solubility in these solvents. Such vulcanized compounds can, by prolonged heating, be brought into solution in various solvents, but there is this distinction, that, in the latter case, the solution is accompanied by a depolymerization, and evaporation of the sol-

[1] There is such a diversity of opinion concerning the best method for any single determination, and since the interpretation of the analysis, rather than the absolute results obtained, is the more important of the two, it must necessarily follow that the results of the analysis are inseparable from the method by which they were obtained. It is not sufficient merely to say that a sample has 3.00% of sulfur, it must be stated that it has 3.00% of sulfur when determined by a certain method. This has been one of the glaring weaknesses of the average specification in this country, and has been the cause of a great deal of controversy and actual financial loss.

vent will not give us the rubber in the same condition in which it existed before solution. Rubber containing only a small quantity of combined sulfur is tough and elastic, but as the percentage of combined sulfur increases, the degree of extensibility becomes less and less, the rubber becomes harder until we obtain the familiar substance, vulcanite, or hard rubber, and the limit of sulfur addition is found at $(C_{10}H_{16}\,S_2)_x$. To effect the combination between the rubber and sulfur, catalysts are employed, both organic and inorganic, while to produce the desired properties in the finished article, various oils, waxes, gums and pigments are added.

It would seem, therefore, to be quite apparent that in order to understand the analysis of rubber, one must be familiar with the materials which enter into the rubber compounds, the chemical changes which take place during vulcanization, as well as merely the analytical methods. In this way, the analysis may be directed towards bringing out the really important points in the rubber compound. The general scheme which has been adopted, is to first present a description of the raw materials, the methods, and the theories of vulcanization. This will be followed by directions for sampling, general and specific methods of analysis, and finally some suggestions for interpreting the results of the analysis, with the view to reconstructing the formula of the rubber compound.

Chapter II.

The Composition of Crude Rubber.

Crude rubber is obtained from various trees, shrubs, or vines. Some of these grow wild, and others are cultivated for the sake of their yield of rubber. Twenty years ago cultivated or plantation rubber was practically unknown; the crude rubber of that time was obtained from all quarters of the tropical world, Brazil furnishing the greater portion of the wild rubber. Not only did Brazil furnish the major part of the rubber, but it was also the best in quality, largely because of the care taken in preparation, and the uniformity achieved in spite of the rather crude methods which were employed. One reason for this uniformity was that most of the rubber was obtained from a single species, the *Hevea Braziliensis,* which today is not only the source of the best wild rubber, but, through transplanting, is also the chief, one might almost say the entire, source of the plantation rubber as well. The *Hevea* rubber became known commercially as Para rubber, from the port from which shipments were made.

Para Rubber. Two main subdivisions are made in Para rubber, the Up-river, and Islands. The former comprises rubber collected in the inland section, along the Amazon river and its branches. The Islands rubber is so named because it is largely collected in the islands of the delta of the Amazon, and the adjacent country. There are subdivisions of the main group, the Up-river including Acre, Bolivian, Madeira, Manaos, etc., and the Islands rubber is similarly subdivided.

Rubber comes from the latex of the trees, and the latex is gathered by making a number of small cuts extending just below the bark. The latex flows from these cuts, and is caught in small cups. The rubber gatherer collects the latex daily, takes it to his hut, and prepares it for the market by the process of coagulation and smoking. A paddle is dipped into the latex, and the thin film which remains on the surface is coagulated by holding it over

the smoke from burning uri-curi nuts. The heat and smoke break down the emulsion, separating the rubber from the so-called serum of the latex. Much of the serum drips out, but a considerable portion is retained, and the solids contained therein become a part of the crude rubber, profoundly influencing the vulcanization and the physical properties. The operation of dipping (or the latex may be poured over the paddle) and smoking is continued until a fair sized ball is obtained. The rubber so prepared is called Fine Para, but if for any reason fermentation or oxidation should set in, and the rubber become sticky, it is classed with the lower grades. The scrap from the cups, buckets, and from the bark of the trees, is gathered together, and called "Coarse Para." The shape and general appearance of these "balls" varies widely, but the method of preparation is the same throughout, so that there actually exists a remarkably uniform method of preparation throughout the entire territory where the Para rubber is gathered.

Castilloa. Second among the wild rubbers is that obtained from the *Castilloa Ulei* or *Castilloa Elastica* which produce the kinds known as Caucho, Centrals, etc. This rubber is coagulated in bulk, is not smoked, and appears on the market as balls, sheets, strips, or slabs. It is subdivided into grades, but, even in the best, there is nothing like the uniformity of quality which one finds in the Para rubber.

African Rubbers. African rubbers are largely gathered from vines, chiefly the *Landolphia*, with innumerable sorts and grades many of which are quite indistinguishable, even to the expert, and certainly cannot be identified after vulcanization. Some African rubbers are prepared according to methods peculiar to the place, by means of which they can be identified, or they may gather from the means by which they are coagulated an odor peculiarly their own, but the differences from one lot of the same name to the next is frequently greater than that between two entirely different sorts. During the past year there has been a decided diminution in the quantity of African rubber produced, and many sorts have entirely disappeared from the market as their quality is so poor that the price they will bring on the present day markets is not sufficient to pay the cost of collecting. If the Plantation rubber continues to increase at anywhere near the rate it has for the past eight or ten years, it will mean such a low

standard market price for the best grades of rubber that the poorer African sorts will disappear altogether. From the experiences which the manufacturers have had in trying to produce uniform quality material with such stuff, we may surmise that no tears will be shed at the loss.

Guayule. Guayule is the rubber obtained from the shrub *Parthenium Argentatum,* found extensively in Mexico and Texas. This rubber is not obtained in the form of a latex, but the plants are cut down, and the rubber which exists in the stems, leaves, and branches of the plant, is separated by mechanical or chemical means, or both. The crude Guayule thus obtained runs very high in resins and other impurities; indeed, these form about two thirds of the crude rubber. It usually undergoes a process of purification, or deresinification in order to prepare it for the market, whereby the rubber hydrocarbon content is raised to somewhere around 75%, or even higher. Guayule is a soft, sticky, stretchy rubber, retaining these properties to a high degree even after vulcanization, and it finds its chief use as a constituent of frictions.

Pontianak. Java, Borneo, and the neighboring countries, produce a tree, the *Dyera Costulata,* which yields a product containing about 90% of resins and similar substances, and about 10% of rubber. This mixture is known chiefly as Pontianak, or Jelutong rubber. In the crude form, it is quite hard, owing to the high resin content, and particularly to the nature of the resin. In the process of purification of crude Pontianak, a large part of this resin is removed, and is marketed separately. Pontianak resin finds some use in rubber mixings; it is hard, brittle resin, with a conchoidal fracture, very much resembling our ordinary rosin. It is soluble in acetone, chloroform, benzene, and other organic solvents, and consists largely of unsaponifiable hydrocarbons. Ellis and Wells[1] find that on heating, the solubility of the resin and the percentage of unsaturated compounds increase. While there is some demand commercially for this resin, it does not appear to be sufficiently extensive and remunerative to permit much Pontianak rubber to come to this country. At the present prevailing market prices, it seems obvious that the rubber portion must be handled as a by-product only.[2]

[1] J. Ind. Eng. Chem. 7, 747-50 (1915).

[2] As an indication of the disappearance of Pontianak rubber from the market, it is only necessary to note that according to reasonably reliable statistics, only

When the resin content is materially reduced, Pontianak rubber is very tacky, and plastic, making it difficult to store, as it has the tendency to flow together to form one huge, unmanageable mass.

Plantation Rubbers. The development of the *Hevea* on the plantations of the Far East, has reached such proportions as to make it the dominating feature of the rubber market. Fifteen years ago, plantation rubber was of small commercial importance, very little of it being produced. Today, the plantations furnish fully 80% of the world's supply. The rapidity of the growth is well illustrated in the following figures, which while they may not be absolutely accurate, are sufficiently so to show the rapidity of the growth of this phase of the industry:

Production of Plantation Rubber.

	Tons
1903	25
1904	50
1905	150
1906	500
1907	1,000
1908	2,000
1909	4,000
1910	8,000
1911	15,000
1912	30,000
1913	50,000
1914	75,000
1915	110,000
1916	160,000
1917	225,000
1918	190,000
1919	360,000

The time has arrived when cultivated rubber can be produced so cheaply that the poorer grades of wild rubber have been forced out of the market, and even the better grades have suffered severely. The analyst may therefore expect less and less to be confronted with samples for analysis which have been made up wholly, or in great part, of wild rubbers. Only in the Para grades does there seem to be any sort of adherence to the old grades of wild rubber. There are still some specifications for various materials, which insist upon the use of Fine Para rubber (although unless some representative of the purchaser actually sees the

1000 tons were imported during 1921. During the same period, crude rubber imports were estimated to be between 275,000 and 300,000 tons. In 1905-6, the ratio of imports was 2 tons of crude rubber to one ton of Pontianak.

material made, how they are going to distinguish good smoked sheets from Fine Para is more than one can say), and they are unwilling to change over to plantations because they do not know what the effect of such a change would make on the life of the articles. Some rubber specialties have been made from the same formulas, calling for Para grades, for a number of years, and still continue to be made in this fashion, although at times it is difficult to get just the grades of wild rubber needed.

Smoked Sheet. Although at times it does not command the highest price, it is the standard grade of plantation rubber.[3] The rubber should be clean, dry, firm, of a good color and free from more than traces of mold or rust. The moisture content will vary between 0.3% and 1.0%. The acetone extract will usually be between 2.5% and 3.0%, and almost always will be below 4%. The ash should be negligible.

Pale Crepe. Pale crepe is frequently called first latex, although the same latex may, at the choice of the plantations, be made into either ribbed smoked sheet, or pale crepe. The latter is usually cleaner than smoked sheet; chemically, they are very much alike. The moisture content will average lower than smoked sheet, the ash is negligible, and the resin content between 2.5% and 4.0%.

Smoked Crepe. Smoked crepe is usually cleaner than smoked sheet (the latter frequently contains bark, etc.), with a lower moisture content, approaching that of pale crepe. The resins seem to run about the same; if anything, a bit higher than the average of smoked sheets. No other particular differences have been noted.

Amber Crepe. Amber crepe comes in several grades, according to color. There is no sharp dividing line between these grades and the pale crepe, or even amongst themselves. Some of the lighter amber crepes are very much like the poorer lots of pale crepe. The resins, moisture, and ash in the paler colored amber crepes is about the same as for pale crepe or smoked sheet; the lower grades are apt to be sticky, run high in dirt and moisture, and by reason of surface oxidation, they may be tacky and show a higher acetone soluble figure.

Roll Brown Crepe. Roll brown crepe comes into the market

[3] For the methods of preparation of Smoked Sheet, and Crepe, cf. Whitby, "Plantation Rubber, and the Testing of Rubber."

in the form of sheets of crepe which have been rolled up into small bundles about 5 to 6 inches in diameter, and about 10 to 15 inches in length. It is the lowest grade of plantation rubber on the market, is very tacky, and dirty, and must always be washed in the factory before it can be used. When washed clean, and dried, it replaces acceptably the wild rubbers which have been used in friction stocks, such as Guayule, etc.

Constituents of Crude Rubber, Other Than the Rubber Hydrocarbons.

We have already drawn attention to that portion of the crude rubber which is soluble in acetone, and which is known commercially as rubber resins. Apart from the dirt, bark, and water, which may be included in crude rubber, but which we cannot consider as anything but contamination, there are some other substances, which are not rubber, but are nevertheless found in all crude rubbers.

Resins. *Hevea* rubber contains, in addition to the rubber hydrocarbons from 2% to 4% of resins. These resins are about 80% saponifiable, and 20% unsaponifiable. They are soluble in acetone, alcohol, chloroform, and many other organic solvents. The solution is usually a pale yellow color, and the residue, when the solvent has been driven off, is light colored with the consistency of butter. In the unsaponifiable portion, Whitby[4] has identified some five substances from the unsaponifiable portion, some of which show optical activity, and some give sterol reactions. The acetone extract of *Hevea* rubber may go higher than 4%, but this does not necessarily mean that the resin content is high, but rather that there has been oxidation and depolymerization of the rubber, producing by-products which also are soluble in acetone.

Insoluble Matter. If we take a sheet of pale crepe, smoked sheet, etc., and dissolve it in gasoline, being careful not to shake too much, we will find flakes of the crude rubber which will not dissolve. This is what is known as the "insoluble matter." The amount will vary with the method of preparation; analyses have run between 2% and 6%. Rubber prepared by the total evapora-

[4] Paper read at the Spring meeting of the American Chemical Society at Rochester, April 1921. "Contribution to the knowledge of the resins of *Hevea* rubber," by G. Stafford Whitby and J. Doolid.

tion of the latex will have the highest figure, whereas the ordinary methods of coagulation with acetic acid, washing, etc., reduce this figure considerably. The insoluble matter resembles the proteins, and, according to Eaton, its fermentation will permit the formation of nitrogenous decomposition products which act as accelerators of vulcanization. Such reactions take place in the so-called slab rubber, in which the coagulum is only slightly pressed, and which retains a large amount of the non-soluble substances in the latex.

While the insoluble matter may be shown by treating the original sheet with gasoline as described above, it is next to impossible to wash out all of the rubber, so that we cannot depend upon this separation as a means of a quantitative separation. The nitrogen factor is obtained by dividing the weight of the nitrogen-containing substance by the nitrogen it contains; one determines the nitrogen and multiplies by this factor to arrive at the total amount of nitrogen-substance present. This factor varies considerably, but 6.25 is a fair average, and will give results near enough to the truth to be acceptable for all practical purposes. In the determination of glue by the Kjeldahl method, this insoluble matter appears as a conflicting element in the determination, and must be taken into account.

The best rubbers are clean and dry, and have practically no ash. A high ash indicates a rubber which has been poorly washed or which has since picked up dirt, sand, etc.

There are usually small amounts of substances, whose composition we do not know, but which we recognize by the fact that they act as accelerator of the vulcanization process. In amount, they are negligible, except in the case of compounds composed entirely of rubber and sulfur, when their presence or absence may bear an important part in securing the proper degree of vulcanization.

Tests for Crude Rubber.

Crude rubber may contain dirt, bark, moisture, resins, proteins, and oxidized or depolymerized rubber. Bark, dirt, moisture, and any water-soluble substances, are grouped together as "loss on washing."

Loss on Washing. For plantation rubbers, in which the moisture and dirt is usually very low, a 5 lb. to 10 lb. sample will suf-

fice. The sample should be taken in small pieces from different parts of the lot, and at least every five cases should be sampled. If the sample thus taken proves to be too large to handle, it can be weighed, broken down on the mill, and a smaller sample taken from this broken down rubber. The latter should be weighed when cool, in order to ascertain whether or not any loss in weight has taken place. For wild rubbers, not less than 50 lbs., and preferably 100 lbs. should be taken for the loss in washing test; afterwards, for the other determinations, a smaller sample may be drawn from the washed and dried rubber. Even greater care must be exercised in sampling wild rubber, because of the unevenness in size, cleanliness, moisture, etc., of the various balls or lots of wild rubber. Fine Para, for example, may be sampled by cutting the balls into quarters, until about 50 lbs. are obtained. Dirtier rubbers, or those which will vary more from lot to lot, should be sampled up to 100 lbs. In a later chapter, we propose to deal more at length with this subject of sampling, but suffice it to say here that unless the proper care is exerted to make the sample drawn for this test one which is of the same average quality as the lot, the entire work of testing is worse than if it were not done at all, for it may lead to totally false results. The rubber should be washed immediately after the sample has been drawn and weighed.

Plantation rubber may be washed directly, without any previous treatment; wild rubbers should be heated in hot water to soften them, and render them more plastic, so as to facilitate the operation. The rubber is washed in the usual factory manner, and then dried in a vacuum dryer. After removal from the vacuum dryer, the rubber is cooled, and weighed, and the loss noted.

A new sample of about 1000 grams is taken from different parts of the washed and dried sample, and united by passing several times through a laboratory mill. Five grams are weighed out, sheeted thin on the laboratory mill (care must be taken to see that no mechanical loss occurs), and dried to constant weight at 100C. A laboratory vacuum oven may be used, but the temperature should be less than 100C, since with the reduced pressure the higher temperature is not necessary, and there is less likelihood of damage to the rubber at the lower temperature. The loss on drying the 5 gr. sample, plus the shrinkage during washing,

gives the total loss in weight, and should be calculated to percentage, based upon the original weight of the sample.

Resins. Sheet out thin, 5 gr. of rubber,[5] calculated to the dry basis, and wrap in filter paper which has previously been extracted with acetone, place in the extraction flask,[6] and extract continuously with acetone for eight hours. Remove the solvent, dry the flask and contents to constant weight at 90C and calculate to percentage. The color, hardness, and odor of the extract should be noted.

Moisture. It is sometimes desirable to know simply the moisture in the original sample. This is not practicable with most wild rubbers, where the moisture is very unevenly distributed, but with plantation rubbers it is quite feasible, and often a valuable figure.

Cut up 5 grams into small pieces, dry to constant weight in an inert atmosphere at 90C. Calculate to percentage.

Nitrogen. A 1 gr. sample is placed in a Kjeldahl flask, with 10 gr. of potassium sulfate, 50 cc. of conc. sulfuric acid and 1 gr. of copper sulfate. Heat for three to four hours (it is not necessary for the solution to become clear), transfer to a distilling flask, make the solution alkaline with caustic soda, and distil the ammonia into standard sulfuric or hydrochloric acid. Titrate the excess of acid with standard sodium carbonate, using methyl orange or methyl red as indicator.

Various determinations on the amount of nitrogen in the insoluble matter, have given figures ranging between 12% to 16%.[7] The usual factor of 6.25 will give a conservative figure for the proteins, but it is likely that 8.0 or even higher, may frequently be the more correct value. It will be seen from these figures that the determination of nitrogen does not signify very much.

Curing Tests. It is desirable not merely to know the chemical composition and the loss on washing of crude rubber, but also to know something of its vulcanizing properties. For this purpose, a standard formula should be employed, a series of cures made from this mix, and stress-strain curves drawn for each cure.

[5] It is convenient, if not pressed for time, to take the dried rubber from the moisture determination in loss on washing. This simplifies the correction, but in so doing, it must be seen that the sample has not been altered during the drying, by oxidation, or depolymerization.

[6] Cf. Acetone extraction, under methods of analysis, page 68.

[7] Cf. Schmitz, Gummi Ztg. 27, 1085. 1131; Spence and Kratz, Koll. Zeit. *14*, 268-77 (1914).

The question of a standard formula is one which may not be dismissed lightly. At present, many of the plantation and factory chemists are using a mixture of rubber and sulfur. This, however, is open to serious objection,[8] and a less objectionable procedure, even granting that the formula itself may not be the best one, or most suited for all work, is to use a formula containing a small amount of zinc oxide, and sufficient accelerator and sulfur to produce satisfactory cures. One such formula would be: hexamethylenetetramine 0.5%, sulfur 4.5%, zinc oxide 5%, rubber 90%. This mixture contains enough sulfur for a coefficient of 5.0,[9] which is higher than one would ordinarily go, and zinc oxide in excess of that required to neutralize any organic acids in the rubber, and provide a basic mix for vulcanization, since practically all organic accelerators seem to work better under such conditions.[10] Particular pains should be taken regarding the quality of the zinc oxide, sulfur, and accelerator; they should be of C. P. grade, and not just the commercial stuff used in the factory. Such grades are to be found in the market, and are worth the extra cost. It is not without the bounds of reason that much of our unexplainable vagaries in rubber testing is really traceable to the impurities in the pigments, and not to the rubber itself.

Needless to say, perhaps, the results depend largely on the cleanliness and technique in mixing and curing, the accuracy of the thermometers, and the accuracy of the testing machines. No tests should be made until at least 48 hours after vulcanization.[11]

[8] *Cf.* J. B. Tuttle, Variability of Crude Rubber, J. Ind. Eng. Chem. *13*, 519-22 (1921).

[9] The sulfur coefficient, sometimes called the coefficient of vulcanization, is the ratio of combined sulfur to the rubber. It is calculated by dividing the percentage of rubber by the percentage of combined sulfur.

It may be mentioned that the coefficient of vulcanization necessary to produce identical physical properties in two or more compounds, is not a constant, but varies with the amount and nature of the accelerator employed, and to a lesser extent on the other constituents of the compound.

[10] The real purpose of the use of the added organic accelerator and the zinc oxide should not be lost sight of in any discussion of the advisability of using this or any similar formula. It has been shown that crude rubber contains varying amounts of natural organic accelerators, and we must eliminate their effect if we are to study the actual variation of the rubber itself.

[11] There are some who believe that 24 hours is sufficient to permit the rubber samples to reach equilibrium. At times, we have taken samples from the vulcanizing press, and after cooling in running water. tested them immediately. But where results of today are to be compared with those of the past, or with those to be obtained in the future, the only safe procedure is to allow the full 48 hours, so that such comparisons as may be made will be made under identical circumstances, and any differences noted will be real ones, and not those caused by the fact that at times samples had not yet reached equilibrium.

Chapter III.

The Preparation of Rubber Compounds.

The art and science of preparing rubber compounds is something which may well deserve treatment of its own. It is not the intention to explore the whys and wherefores of the matter, for many of the commercial compounds just "grew up" as time went on, a little of a new material here, and a little less of an old one there, until at present they are so complicated that even the owners of the formulas are afraid to make any further alterations. On the other hand, we have a very large number of formulas which have been constructed on the basis of the definite physical and chemical properties of such a mixture as determined by years of research. Irrespective of why it was used, the analyst is primarily interested only in what materials are likely to be used.[1] Moreover, it is utterly impossible to include every article which has ever been used in rubber manufacture, but only those which have really attained some commercial importance, and hence are likely to be encountered in an analysis.

Crude Rubbers. In the preceding chapters, the general properties of the most important crude rubbers were given. This is probably as good a time as any to draw attention to the fact that seldom will one find a single kind of crude rubber in a rubber compound. Coarse Para will be mixed with Fine Para, or amber crepes will be mixed with smoked sheets or pale crepe. It may

[1] At the time of writing, the situation with respect to crude rubber is such that the preparation of a new compound is a more than usually serious problem. With the best grades of plantation rubber selling around 15 cents a pound, the saving in the use of reclaimed rubbers and substitutes is questionable, if we consider that such materials are to replace the rubber. Some reclaimed rubbers may have an added value on account of the active fillers, such as zinc oxide and gas black or lamp black, which they may contain; or we may use reclaims and substitutes in special cases on account of special properties which they impart. However, it is incredible that such conditions as now prevail are to continue indefinitely, and hence we are proceeding on the basis that the normal price for crude rubber will be from 25 to 30 cents (if not higher), and at this price the use of certain grades of reclaims and substitutes will effect savings in costs, and hence the analyst may expect to find them in examining manufactured articles.

seem superfluous, but it is safer to call attention to the fact that replacing Fine Para with Coarse Para, or smoked sheet with amber crepe, is merely a matter of economy; the rubbers used are not as good as those they replace, and the quality of the compound is lowered. It is purely a question of deciding whether or not the properties of the compound are sufficient to meet the demands of the service. On the other hand, rubber such as Pontianak, Guayule, roll brown crepe, etc., when used as softeners, are used independently of their cost, and their use has continued in many cases when they cost practically as much, or even more than the so-called better rubbers. These points are worth bearing in mind in figuring out the probable formula from the analysis of a rubber compound.

Reclaimed Rubber. We have seen that the rubber hydrocarbon can combine with sulfur until the compound $(C_{10}H_{16}\ S_2)_x$ is reached, when the ratio of rubber to sulfur is 136:64. In the ordinary soft vulcanized articles, the sulfur coefficient is between 1.5 and 5.0, depending upon the type of accelerator, and the degree of vulcanization. Such material is able to take up further quantities of sulfur to form a new compound with a higher coefficient, which, while somewhat harder than the material from which it was made, may still be of service. Each addition of sulfur, other conditions being equal, produces a harder product than before, until, with the maximum amount of sulfur which may be added, we reach the product ebonite. The hardness of the rubber itself is frequently lessened by the admixture of softening oils, and the partial depolymerization which takes place produces a soft and tacky substance, which also helps to counteract the hardening effect of the additional sulfur.

Before vulcanized rubber can be used a second time, it must be put into condition to be mixed in a homogeneous manner with new rubber. There are two general processes employed, (*a*) the acid reclaiming process; and (*b*) the alkali reclaiming process. These processes serve to remove any fabric which may be present, the free sulfur, and, of course, some of the fillers, both organic and inorganic. In the latter case, the amount and nature of the fillers removed will depend largely upon the process which is used and the chemical nature of the fillers. Zinc oxide and whiting are largely removed in the acid process, zinc oxide to a slight extent in the alkali process, while gas black and lamp black are

unaffected by either. Oil substitutes are not attacked in the acid process, but are almost completely removed by the alkali process.

These processes of reclaiming do not reverse the vulcanization process; on the contrary, if there be any quantity of free sulfur present, part of it will combine with the rubber during the reclaiming, the sulfur coefficient being higher afterward than before. Other processes have been worked out for the purpose of taking out the sulfur and restoring the double bond, in which case we would expect a product similar to new rubber, and which would vulcanize in the same manner. This is the ideal towards which the researches have been directed, but it must be admitted that as yet we have fallen far short of the ideal, and the reclaimed rubber encountered in vulcanized compounds has been made by one or the other of the two methods mentioned above, or some variation of them.

Reclaimed rubber is added, under normal market conditions, first of all because it is cheaper. Certain grades may be used because they give desirable properties; for example, vulcanized reclaimed rubber resists oil better than does new rubber, and the use to which the article is to be put is worthy of notice in deciding whether or not reclaimed rubber has been used on account of its cost, or because in the case in question, it is actually better.

In the manufacture of pneumatic tires, there is always a considerable amount of fabric trimmings, containing a large amount of new, unvulcanized rubber. By the acid reclaiming process, the fabric may be entirely removed, with a considerable portion of the sulfur, without appreciably causing the rubber and sulfur to combine. The product, known as "reclaimed or pure gum friction," is a valuable adjunct in rubber compounding.

Oil Substitutes.

In the preparation of certain articles, where the highest physical properties were not of primary importance, substitutes for rubber have been used in order to lessen the cost of manufacture (cf. footnote, page 26). One group of such substitutes is made from oils of various kinds, and these substitutes are known commercially as "oil substitutes."

When drying, or semi-drying oils, such as linseed, soya, corn,

cottonseed, and similar oils, are treated with sulfur or sulfur chloride, a solid plastic mass is obtained. These products have been called vulcanized oils, because of the similarity of the processes of preparation with those of rubber. The reaction with sulfur requires heating, and the product varies in color from a light to a very dark brown, or even black. The sulfur chloride combines at ordinary temperatures, giving us the so-called "white substitutes."

Mixed with these substitutes are various gums and oils, producing an almost endless number of combinations. This need not bother the analyst, however, for the treated oils are insoluble in acetone and chloroform, whereas the untreated oils and gums are usually soluble in one or the other of these solvents. They may also be loaded with mineral pigments of various kinds.

Tests of Oil Substitutes.

An examination of the raw material should cover the unchanged oil, loss on heating at 100C, free sulfur, and ash. Unchanged oil acts in a totally different manner from the true substitute, and the free sulfur is especially important, since it is capable of combining with the rubber during vulcanization; hence any free sulfur present must be taken into account when figuring the amount of sulfur to be added as such to the rubber compound.

Unchanged Oil. Reduce the sample to a fine state of division by crumbling or cutting. Extract 2 gr. with acetone for eight hours; dry the extract to constant weight at 90C, cool and weigh.

Free Sulfur. Treat the dried acetone extract with 50 to 75 cc. of water, and 2 to 3 cc. of bromine, heat until colorless, or nearly so, filter through a folded filter; heat the filtrate to boiling, add 10 cc. 10% barium chloride, and determine the precipitated barium sulfate as usual. Calculate to sulfur, and deduct the percentage of free sulfur from the total acetone extract. The remainder is the unchanged oil.

Loss in Weight. Dry a 2 gr. sample in a neutral atmosphere at 90/100C until constant weight is secured.

Mineral Fillers. Ignite a 1 gr. sample, cool the residue and weigh. Pure oil substitutes should have practically no ash; if any pigments are added, the amount will be such as to leave no

doubt in the analyst's mind as to whether such additional was accidental, or not. Oil substitutes are usually found in amounts of from 1% to 5%, although we have seen some German made rubber tubing that had nearly 50% of oil substitute.

Mineral Rubber.

The mineral rubbers are asphaltic or bituminous hydrocarbons obtained either from natural or artificial sources. The natural sources are from the minerals gilsonite and elaterite, while the artificial mineral rubbers are made largely from the blown oils from petroleum residues.[2]

Mineral rubber possesses a melting point above that of the usual vulcanization range, but its plasticity enables it to be worked readily at much lower temperatures. In amounts up to 7 volumes,[3] it materially improves the tensile properties. It serves to soften the uncured stock, makes it tackier reduces blooming, and in a variety of ways proves itself to be an asset to a rubber compound. It improves the waterproofing properties of rubber.

Owing largely to the differences in the source of supply, and to the various methods of preparation, the chemical and physical properties vary widely. The acetone-soluble matter varies enormously, running as low as 17%, and as high as 60%, the higher percentages being the more common occurrence. Chloroform will dissolve part of the residue, equal to about 10% of the whole. They may contain as much as 10% of their weight in sulfur, all of which is chemically combined. There is always a fair sized amount which is soluble neither in acetone nor chloroform.

While the solvents do not give us exact data as to the quantitative figures on mineral rubber, the color of the chloroform extract is a very reliable index in determining the presence or absence of this material. When present, this extract is deep brown to black

[2] For the best and most recent work on Mineral Rubber, consult the article by C. Olin North, "Mineral Rubber," read at the meeting of the Rubber Division of the American Chemical Society at New York, September 6th to 10th, 1921. Abstracts of this paper are to be found in the "India Rubber World." *65*, 191-2 (1921), and "The Rubber Age," *10*, 130-1 (1921).

[3] Since the specific gravity of the materials used in rubber compounding varies widely, it affords a more exact method of comparing the effect of the different substances if they are compared on the basis of volume rather than weight. The volume is referred to the total volume of rubber, the latter being taken as 100.

in color, and is not likely to be confused with any other class of material used in rubber manufacture.

During vulcanization, the percentage of soluble matter may change somewhat; the acetone extract is usually somewhat lower than when the material itself is subjected to extraction. The chloroform extract shows little change. Various explanations have been offered: (1) that the mineral rubber unites with the rubber; (2) it combines with the sulfur to form insoluble products; (3) the dispersion of the mineral rubber on the crude rubber produces an adsorption effect, and renders the former more diffisult to dissolve out of the mix. Of these, the second seems to be the most plausible, although admittedly the other two are possibilities.

Mineral rubber has a specific gravity of about 1.00; the hardness varies according to the melting point. The melting point is anything that may be desired, but the most popular grade is that melting in the neighborhood of 310F.

North[4] has determined that the best results with mineral rubber are obtained when the proportion is 7 volumes of mineral rubber to 100 of rubber. One is more likely to meet with less rather than with more than this amount.

Tests for Mineral Rubber.

Acetone Soluble. Extract with acetone for four hours, a 1 gr. sample of the mineral rubber; dry to constant weight, at 100C.

Chloroform Extract. Without drying the sample which has been extracted with acetone, extract with chloroform for two hours, or longer if at the end of that period the solvent is still colored. Dry the extract to constant weight, at 100C.

Ash. Ignite 1 gr. in a porcelain crucible, cool and weigh. The residue should be negligible.

Insoluble Matter. The difference between 100% and the sum of the acetone and chloroform extracts, and the ash, shall be called "insoluble matter."

Mineral Hydrocarbons.

The mineral hydrocarbons may be divided into two classes, hard and soft. The former include ozokerite, ceresin, and paraffin; the latter, petrolatum and heavy mineral oil. The hard

[4] Loc. cit.

hydrocarbons are useful for their waterproofing effect, and are to be found largely in materials intended for electrical purposes, such as insulated wire and cable. The soft hydrocarbons are used purely as softeners, to facilitate the handling of the stocks in the factory, and whereas the hard hydrocarbons are without any serious effect on the aging qualities, the soft hydrocarbons have a decided deteriorating effect, and must be used in small quantities. The explanation of this effect would appear to be that the mineral oils are solvents for vulcanized rubber (as previously stated, however, this is not a true solution, but rather a depolymerization preceding solution).

Mineral hydrocarbons are rarely used to a greater extent than 5%, and in the greatest number of cases the amount used is between 1% and 2%.

Ozokerite. Ozokerite is a natural product, found in Austria, Russia and southern Utah. It is dark brown to black in color, with a specific gravity of about 0.90. The melting point should exceed 65C (150F). Ceresin is ozokerite which has been purified by treatment with fuming sulfuric acid; it is pale yellow in color, with a resinous luster, non-crystalline in appearance, but in other respects, similar to the parent substance.

Paraffin. Paraffin is a hard, white, crystalline substance, composed of the higher boiling hydrocarbons from petroleum. Its specific gravity is about 0.90, the melting point almost anything that one desires, from soft paraffin which borders closely on petrolatum, to the hard paraffins with melting points around 60C.

Ozokerite and ceresin are so much higher in price than paraffin, that the temptation for adulteration is very great, and this is all the more true because of the fact that paraffin, which is used largely as the adulterant, is so near in chemical and physical properties that rather large amounts can be added without fear of detection. Ceresin in the pure state is much less crystalline than paraffin, and less brittle, but it is doubtful if these advantages warrant the extra cost of the pure article.

Paraffin and ceresin have the peculiar property of working toward the surface of a rubber article, much in the same manner as sulfur "blooms." It appears within a few days after vulcanization, and if a slab of rubber containing paraffin be left untouched for say six months, it is possible to scrape a considerable quantity of clean paraffin from the surface (possibly mixed with

sulfur if the free sulfur is high). This fact is important in analyzing such materials, for the ordinary handling, cleaning, etc., in preparing a sample for analysis, will remove an appreciable quantity, and hence, on this account, irrespective of the errors of analysis, the determination of paraffin or ceresin is likely to be low rather than high.

Oils and Waxes.

Rubber compounds may be made suitable for calendaring, tubing, and other operations, either by excessive working on the mixing mills, or by the use of elevated temperatures. Both methods are objectionable in one sense or another, the excessive working breaks down the rubber, producing a sticky, porous material which is difficult to handle, to say nothing of its poorer tensile properties. High temperatures are to be avoided in the preliminary stages of manufacture, especially with organic accelerators, since some of the latter become very active at moderately low temperatures, and a partial vulcanization will be effected (what is technically known as "burnt" or "scorched" stock). One method for avoiding these difficulties is to add a small amount of oil (usually 1% to 3%), which softens the rubber compound and brings about satisfactory working conditions. We recognize two classes in these softeners, (*a*) in which the oil or wax acts merely as a softener; (*b*) in which in addition to its softening effect, it adds some distinct and desired property, such as tackiness, etc. In class (*a*) we find palm oil, cottonseed oil, petrolatum or vaseline, and heavy mineral oils; in class (*b*), Burgundy pitch, colophony or ordinary rosin, rosin oil, tar oils, etc. The former may be expected in almost any stock, but the latter are used chiefly in cement stocks, frictions, tapes, etc., where adhesive properties have a particular value.

Palm Oil. Palm oil is obtained from the fruit of the palm tree, *Eloeis guineensis*, and the west coast of Africa is practically the only important commercial source of this oil. Specific gravity, 0.921-0.925; melting point 27-42C, solidification point 37-39C, depending upon the age and origin of the oil. Iodine number, 53-57; the commercial oil contains water, sometimes as much as 7%; other impurities up to 3%. It may be adulterated with bark and dirt, and, before using, palm oil is melted, and the clean oil

skimmed from the surface. Palm oil is rarely adulterated with other oils or fats, hence it is usually sufficient to determine water, total impurities, and the solidifying point. The color varies from orange yellow to a dark, dirty red.

Cottonseed Oil. Cottonseed oil is obtained from the seeds of the cotton plant, *Gossypium,* of which the principal species are *G. Herbaceum* in the United States, and *G. Barbadense* in Egypt. Choice crude oil should be free from water and foots, possess a sweet flavor and odor (i.e., should not be rancid), specific gravity 0.922-0.925; solidifying point 3-4C; iodine number 105-110.

Tests for Cottonseed Oil.

The best known test for cottonseed oil is Halphen's color test, made as follows: 1-3 cc. of the oil is dissolved in an equal volume of amyl alcohol, to this is added 1-3 cc. of carbon bisulfide holding in solution 1% of sulfur. The test tube is immersed in boiling water, and the carbon bisulfide driven off. A deep red color appears in about 30 minutes. The test depends upon the presence of some chromogenetic substances which are destroyed by high heating, so that rubber compounds containing cottonseed oil may not show this test after vulcanization.

Petrolatum. Petrolatum, or vaseline, may be either light or dark colored. Its specific gravity is between 0.85 and 0.90. At ordinary temperatures, it is a soft paste, but at 40 to 50C it melts to a clear fluorescent oil. It is not altered in composition during vulcanization, and, unlike paraffin, it remains distributed throughout the compound after vulcanization, and does not bloom to the surface.

Heavy Mineral Oils. The heavy mineral oils are purely softeners, but are more likely to be found as component parts of reclaimed rubber and substitutes, than actually added to compounds as such. They act in practically the same manner as petrolatum.

Burgundy Pitch. Burgundy pitch is more important for its adhesive properties than as a softener, although it acts in both capacities. It is a dark, brittle substance, with a resinous luster, and a specific gravity of about 1.10. It is soluble in acetone. It is obtained from the Norway spruce, *Picea Excelsa,* by scarification of the trees, and collecting the resin after it has hardened.

The volatile oils which are present in the crude resin are removed by boiling with water. It contains considerable bark and dirt, and must be purified by melting and filtering through sieves. It is frequently found in low grade frictions, insulating tape, cements, etc.

Burgundy pitch is composed largely of abietic anhydride, and gives a positive reaction with the Liebermann-Storch test. It is so near ordinary rosin in composition that the latter is frequently used as an adulterant, and it is one that is exceedingly difficult to detect.

Rosin, or Colophony. Rosin is the residue remaining in the still in the separation of oil of turpentine from crude turpentine. Its principal constituent is abietic anhydride. Rosin is about 90% saponifiable, the remaining 10% consisting of rosin oil. It melts anywhere from 100 to 140C, specific gravity 1.08. Its color varies from water white, pale amber, to black, but only the lighter amber colors are used in rubber manufacture. It has very little softening power, but is exceedingly tacky, so that it can be used only in small amounts in cements, frictions, and varnishes.

Rosin Oil. By the destructive distillation of rosin, we obtain, amongst other products, a reddish colored oil, commonly called rosin oil. Its boiling point is around 360C, or over, specific gravity 0.98-1.10; it usually contains 10% to 20% of rosin, which is saponifiable, but the remaining 80% to 90% is an unsaponifiable hydrocarbon. It will be noticed that rosin always contains a small amount of rosin oil, and vice versa, hence, both substances give the same positive reaction in the Liebermann-Storch test.[5]

Rosin oil adds very little to the tackiness of the rubber, and is essentially a softener. It improves the waterproofing qualities of rubber.[6] Rosin oil is not used very extensively, especially in

[5] The simplest way to make this test is to warm a few drops of the oil in 1-2 cc. of acetic anhydride, cool, and to a few drops on a porcelain test plate, add a drop of sulfuric acid of sp. g. about 1.5. A reddish violet color indicates rosin or rosin oil. It is believed that the unsaponifiable portion is really responsible for the color, and when examining for rosin or rosin oil, the test may be made much more delicate by making it upon the unsaponifiable portion. Burgundy pitch. Venice turpentine and similar resins, give practically the same color, so that the identification as rosin or rosin oil is not absolutely positive.

[6] Rubber compounds are so frequently used for waterproofing and in such articles as rubber tubing, hot water bags, etc., that one is quite likely to overlook the fact that rubber takes up a large amount of water when left in contact with it for any length of time, and this holds true even after the rubber has been vulcanized. Pure gum sheet, vulcanized, has been found to absorb as much as 20% of its weight in water. C. O. Weber, in his book on India

high grade goods, since it is a solvent, or rather a depolymerizer of rubber. The connection between the two substances, rosin oil and rubber, can readily be seen in the fact that crude turpentine is composed largely of the terpenes sylvestrene and australene, the composition of which is $C_{10}H_{16}$; which form tetrabromides, ozonides, and polymerize easily.

Tar Oils. The tar oils are the residues from the destructive distillation of wood or coal, the coal tars being the ones generally used. They are of varying composition, and act merely as softeners. As a rule, they are soluble in acetone and alcohol, and have a specific gravity of about 1.00. Their properties depend largely upon the source of the crude material, and the degree of rectification.

Glue. The glue used in rubber compounding is the ordinary granulated bone glue. The moisture content varies between 7% and 12%, and the specific gravity is about 1.25. Just as it comes, it may be mixed directly with rubber on a fairly warm mill. It is best to have the mixture refined while it is still hot in order to thoroughly break up any particles of glue. Several other methods are in vogue; 3 parts of glue are heated with 1 part of water until a smooth mixture is obtained,[7] then cooled until it sets to a firm jelly. This is mixed with rubber, and dried in a vacuum dryer. In other preparations, the glue is melted and mixed with oils or glycerin, and then allowed to cool; or it may be dissolved in water, gas black or other fillers stirred in, the solution concentrated, and the cooled mass mixed with rubber.

The effect of glue on rubber is to reduce the elongation, and increase the permanent set. In many compounds, it has been found to exert a stabilizing effect on the cure, flattening out the

Rubber and its Analysis, p. 14, says: "The water absorption of vulcanized rubber is extremely small, certainly not large enough to appreciably affect the insulation of a rubber cable after 5 years' continuous immersion." Weber did not state what kind of a compound he had in mind when he made this statement, but we have had experience with 40% fine Para compounds, containing about 2% of paraffin, which became absolutely waterlogged after about two or three years continuous immersion in water, and were utterly unfit for their purpose. To secure the best waterproofing properties, we resort to the addition of oils, waxes, and pitches. This is particularly true in electrical supplies.

[7] At this stage, several possibilities are open. Some add formaldehyde in sufficient quantities to produce an insoluble glue. Others have added glycerin, about 5% of the dry glue, and concentrated the solution until the moisture content is from 15% to 20%. The purpose of this is to prevent the glue, on cooling, becoming hard and brittle. This glue-glycerin-water combination mixes readily with rubber, and in so doing, the moisture content is substantially reduced.

peak of the vulcanization curves, and reducing the danger of either over or under cures. It has a special field in rubber tubing for conducting gasoline, and other organic solvents, reducing greatly the effect of such solvents on the rubber. Glue has a slight accelerating effect on the vulcanization.

Other Organic Fillers. A large number of organic substances are used in special articles, by reason of the real or fancied improvement in the quality or service, from such addition, or for reasons of economy. Rubber soles may be stiffened with ground cotton fabric; shellac, hard gums and resins are used in cements and in waterproofing; ground cork or leather in some floor coverings, etc., etc.

Vulcanizing Materials.

Sulfur. The sulfur used in rubber should be dry, and free from acid, sand, or other impurities. Before using, it should be carefully sifted through a 50 mesh screen, excepting, of course, in low grade compounds, where such refinements are of no value. The purpose of the sifting is to remove dirt, splinters of wood, etc., that may come from the container, and to remove agglomerations or lumps of sulfur.

Tests for Sulfur.

Acidity. Ten gr. of the sample is placed in a flask, with 100 cc. of distilled water, heated on the water bath for 15-30 minutes, and any acidity titrated with N/10 sodium carbonate, using methyl orange as the indicator. A blank is run on the water used. Not over 2-3 drops should be required to make the solution alkaline.

Moisture. Dry at 85C for one hour in a neutral gas, 1 gr. of sample, cool and weigh. The loss should be negligible.

Ash. Ignite 1 gr. of sulfur in a porcelain crucible, performing the burning in a hood with a strong draft. Cool the crucible and weigh. The ash should be less than 1 mg.

Sulfur Chloride. The sulfur chloride used in rubber manufacture is the monochloride, S_2Cl_2. Since, however, chlorine acts on the monochloride to give the dichloride, there is usually some of the latter present in commercial sulfur monochloride. Pure sulfur monochloride has a specific gravity of 1.709, boils at 138C, fumes strongly in the air, is decomposed by water forming sulfur

dioxide, sulfur and hydrochloric acid. The sulfur liberated by the reaction with water is readily dissolved by the sulfur chloride. It is usually a red or a deep orange color. The dichloride, SCl_2 has a specific gravity of 1.62, boils at 64C, and at the boiling point partially decomposes into S_2Cl_2 and Cl_2.

The commercial sulfur monochloride usually has a gravity between 1.65 and 1.70, and a boiling point between 115C and 130C.

Sulfur monochloride should be stored in a cool, dry spot, in clean earthenware jugs with tight fitting earthenware stoppers. It should not be exposed to the air, on account of its affinity for water.[8]

Organic Accelerators.

The number of organic substances which accelerate the vulcanization of rubber is so great that we have deemed it quite unnecessary to attempt to deal with those which are only of casual interest. Primarily, we are dealing with the analysis of rubber goods, and are chiefly interested in the accelerators which are now being used commercially, or which show possibilities of becoming such. The most widely used organic accelerators today are aniline, thiocarbanilide, and hexamethylenetetramine, and the analyst should look first for these three before proceeding further.

Most organic accelerators are used in small amounts. For very fast curing purposes, such as tire repair stocks, the quantity may be as high as 5% or 6%; but for ordinary compounds the amount is usually 1% or less of the amount of rubber present. The amount used depends largely upon the time of cure desired, and the nature of the accelerator.

Aniline. Aniline, or phenylamine (commonly called aniline oil), is colorless when freshly distilled, but on standing, acquires a deep red color, and this is the condition in which it is found commercially. It is an oily liquid, specific gravity 1.02, boiling point 184.4C, melting point -6C. The melting point is a particularly useful test for purity.

[8] This reaction between sulfur monochloride and water will no doubt explain a considerable amount of the trouble experienced with acid splices, and acid cured goods in general, especially in the hot, sultry days in summer. The evaporation of the solvent of a cement cools the surface below the dew point, resulting in a deposit of a film of moisture. The latter reacts with the S_2Cl_2, reducing the amount of the active vulcanizing substance which, in extreme cases, may be entirely destroyed before any vulcanization has taken place.

Hexamethylenetetramine. A white crystalline powder, commonly called hex, or hexa, melting point about 280C, but decomposes below its melting point. Specific gravity 1.25. It is quite soluble in water, and slightly so in 95% alcohol.

Thiocarbanilide. Thiocarbanilide, diphenylthiourea, $CS(NHPh)_2$, commonly called thio, crystallizes in white plates, M.P. 154C, specific gravity 1.32. It is made by heating carbon bisulfide with aniline. The commercial product is usually a gray powder, and may contain small amounts of sulfur. There are at least a dozen trade names for this one accelerator, some of the preparations being a mixture of thio with inert pigments.

Diphenylamine. Diphenylamine, or phenyl-aniline, $NHPh_2$, has a molecular weight of 169, specific gravity 1.16, melting point 54C, boiling point 302C. It is only slightly soluble in water.

Dimethylaniline. Dimethylaniline, $PhNMe_2$, is a yellow liquid, specific gravity 0.958, melting point 2.5C, boiling point 194C. It is very slightly soluble in water.

Aldehyde Aniline. If well cooled formaldehyde is mixed with aniline, anhydroformaldehyde-aniline (or trimethylenetrianiline) is formed, melting point 140C. In alkaline solution, at ordinary temperatures, formaldehyde and aniline give methylene-diphenyl-diamine, $CH_2(NHPh)_2$, melting at 65C. This may also be prepared by heating anhydroformaldehyde-aniline with alcoholic aniline to 100C.

Commercial aldehyde-aniline is a mixture of several substances, the proportions varying with the differences in the control during the process of manufacture.

Ethylidene Aniline. Ethylidene aniline is made from acetaldehyde and aniline. It is a dark reddish liquid, very stiff at ordinary temperatures, but it becomes quite fluid at the usual working temperatures of the mixing mill (175F-200F).

P-nitrosodimethylaniline. P-nitrosodimethylaniline is obtained in the form of large green, glistening leaflets, melting point 85C. It stains paper or cotton a deep yellow. With caustic alkali, it breaks down into nitrosophenol and dimethylamine, a reaction of much interest in connection with the preparation of the dithiocarbamates.

Other Aniline Derivatives. There are some other derivatives of aniline which might be included here, but are not because they

are of no importance commercially. We may mention p-phenylenediamine, p-aminodimethylaniline, etc.

Diphenylguanidine. Diphenylguanidine, $NH:C:(NHPh)_2$, melting point 147C. It is a mono-acid base; with carbon bisulfide, it forms thiocarbanilide and thiocyanic acid. One commercial preparation consists of two thirds diphenylguanidine, and one third magnesium oxide.

Triphenylguanidine. Two triphenylguanidines are known; (*a*) $PhN:C:(NHPh)_2$, is most easily prepared by heating thiocarbanilide and aniline, and distilling off the excess of aniline. Hydrogen sulfide splits off during the reaction. This is the triphenylguanidine commonly used in rubber compounding. When pure, it exists as white crystals, but the commercial product is frequently colored yellow owing to the excess of aniline which has not been distilled. It has a melting point of 143C. (*b*) The second triphenylguanidine is derived from the HCl salt of diphenylamine and cyananilide, the formula being $NH:C.(PhNH).(Ph_2N)$. It also has accelerating properties.

Diphenylcarboimide. Diphenylcarboimide, $C_{13}H_{10}N_2$; if triphenylguanidine is heated under reduced pressure, aniline is given off and diphenylcarboimide produced, PhN:C:NPh. The crude substance is glassy, resinous, amorphous, with no definite melting point, but softens gradually as it is heated. The pure substance is said to have a melting point of 160C-170C.

Aldehyde Ammonia. When formaldehyde combines with ammonia, instead of following the usual procedure, we get hexamethylenetetramine. Aldehyde ammonia is the product of the combination of acetaldehyde and ammonia; $Me.CHOH.NH_2$; melting point 70C-80C, boiling point 100C. It occurs as colorless crystals, turning dark on exposure to the air; probably on account of the reaction with the moisture in the air, since in contact with water it forms hydroacetamide.[9]

Furfuramide. Furfuramide, formed by the action of ammonia on furfuraldehyde; a light brown crystalline substance, melting point 117C.

Quinoidine. The product sold commercially under the name quinoidine, is the residue remaining after the removal of the alkaloids quinine, cinchonine, and cinchonidine, from the extract of Peruvian bark. It is a dark brown to black resinous solid,

[9] Richter's Organic Chemistry, translation by E. F. Smith, II, p. 206.

non-crystalline, which softens readily, and mixes well with rubber.

Piperidine. Piperidine is a colorless liquid, with a peculiar odor slightly resembling that of pepper; strongly basic, soluble in alcohol and water; boiling point 106C. It is found in nature in combination with piperic acid, as the alkaloid piperine, or piperyl-piperidine, crystallizing in prisms, melting point 129C. Piperine is chiefly of interest in combination with carbon disulfide, when it forms one of the ultra-rapid accelerators (see following).

The So-Called "Ultra-rapid" Accelerators. The combination of carbon bisulfide with secondary amines such as dimethylamine, piperidine, piperine, pyrrolidine, etc., gives rise to the formation of substances which are extremely powerful accelerators of vulcanization; these are believed to be salts of dithiocarbamic acid, and the accelerators of this class are usually called the thiocarbamates. They are so much more powerful than the organic accelerators that some have attempted to distinguish them by the name of "ultra-rapid accelerators."[10]

The dithiocarbamates are mono-basic, and with zinc form salts which form a second class of rapid accelerators.

A third class of rapid accelerators, the thiurams, is formed by the oxidation of the dithiocarbamates; the product is a derivative of thiuramdisulfide, $NH_2C\text{-}S\text{-}S\text{-}S\text{-}S\text{-}CNH_2$; for example, the tetraethyl derivative would be $(CSNEt_2)_2S_2$, a white crystalline substance, with a melting point of 70C. A few of these products may be mentioned as follows:

Dimethylamine and carbon bisulfide; $C_5H_{14}N_2S_2$, m.p. 103C.
Diethylamine and carbon bisulfide, $C_9H_{22}N_2S_2$; m.p. 130C.
Thiuramdisulfide; $NH_2CS.S.S.SC.NH_2$.
Tetramethylthiuram disulfide, $(CSNMe_2)_2S_2$; m.p. ——.
Tetraethylthiuram disulfide, $(CSNEt_2)_2S_2$; m.p. 70C.

The above list includes practically all of the organic accelerators which have reached any commercial significance, and perhaps a few that have not as yet. There is still the derivatives of quinoline, pyrrole, piperidine, and many others. In fact, it may

[10] Some idea of their power to accelerate vulcanization may be gleaned from the fact that a mixture of 50 parts each of rubber and zinc oxide, 3 parts of sulfur, and only 0.1 part of the dimethyldithiocarbamate, will reach its maximum cure in three minutes. Some of the others in this class are even more rapid in this, giving good cures in one minute, with slabs about one sixteenth of an inch thick, hardly time enough for the heat to penetrate to the center of the sheet.

not be going too far to say that any basic organic compound, containing amino, or imino nitrogen, is a promising substance in which to look for accelerating properties.

Inorganic Accelerators.

The inorganic accelerators are practically limited to compounds of two elements, lead and magnesium. Calcium hydroxide has accelerating power, but it can be used in such small quantities, on account of its hardening effect on a compound, that sufficient of it cannot be used to completely accelerate the cure. Sodium hydroxide in small amounts acts as an accelerator, while in amounts in the neighborhood of 5%, it actually retards vulcanization. The lead compounds are litharge, red lead, basic lead carbonate, sublimed white lead, sublimed blue lead, and lead oleate. Magnesium oxide and carbonate are the only magnesium compounds.

Litharge.

Litharge should be clean, dry, pale yellow in color, free from copper; specific gravity 9.37. There should be only small amounts of the dioxide. Litharge is used in quantities of from 5% to 20%. Of special interest is the manufacture of aprons for the protection of workers with radio-active substances. These contain about 90% of litharge, 9% of rubber, and 1% of sulfur, by weight.

Tests for Litharge.

Moisture. Dry 2 gr. of the sample at 105C for 2 hours, cool and weigh.

Lead Dioxide.[11] Treat 1 gr. of the sample in a beaker with 15 cc. of nitric acid, sp.g 1.20. Stir the sample until all trace of red color has disappeared. Add from a calibrated pipette or burette exactly 10 cc. of dilute hydrogen peroxide (1 part of 3% hydrogen peroxide to 3.5 parts of water). Add about 50 cc. of hot water, and stir until all of the lead dioxide has passed into solution. In the case of some coarsely ground oxides, the contents of the beaker may have to be heated gently to effect complete solution. After the oxide has gone into solution completely, dilute with hot water to 250 cc., titrate with potassium

[11] The Chemical Analysis of Lead and its Compounds, by John A. Schaeffer and Bernard S. White, pub. by Picher Lead Co., Joplin, Mo.

permanganate solution having an iron value of about .005. Run a blank on the hydrogen peroxide.

If the permanganate has been standardized in terms of iron, it can be calculated to lead dioxide, using the factor 2.134. From this the total weight of the dioxide can be calculated.

Copper. Dissolve 20 gr. of litharge in dilute nitric acid, and boil until solution is complete. Add 40 cc. dilute sulfuric acid, boil gently for one hour, and allow to cool. Filter off the lead sulphate and wash thoroughly. Nearly neutralize the acid with ammonia, make acid with hydrochloric acid, warm the solution, and pass in hydrogen sulfide. Filter the precipitate, without washing, using some of the filtrate to transfer the last traces of sulfide to the paper. Dissolve in nitric acid, and wash the paper thoroughly with hot water. Add 3 cc. of conc. sulfuric acid, evaporate until the fumes of sulfuric acid are evolved, cool, dilute, and, after standing, filter again, washing with hot water containing a little sulfuric acid. Precipitate the copper in the filtrate as sulfide in an ammoniacal solution, filter, ignite and weigh in a covered porcelain crucible. The residue will be a mixture of CuO and Cu_2S. Since the percentage of copper is the same in both cases, calculate to copper using the factor 0.7988.

Fineness. Determine the residue on a 200 mesh screen, using water to wash the pigment through, and breaking up any loose lumps with a rubber policeman.

Red Lead.

Red lead is a mixture of the monoxide and dioxide, with a specific gravity of 9.07. It should have a bright red color, be clean and dry. The moisture, lead dioxide, copper and fineness may be determined as under litharge.

White Lead.

White lead is the basic carbonate, containing about 80% metallic lead, and 20% of carbon dioxide and combined water. The specific gravity is 6.46.

Tests for White Lead.

Total Lead.[12] Weigh 1 gr. of the sample, moisten with water, dissolve in acetic acid, and filter, ignite and weigh the impurities. Add to the filtrate 25 cc sulfuric acid (1–1), evaporate until

[12] P. H. Walker, Bull. 109, Bureau of Chemistry, U. S. Dept. of Agriculture.

the acetic acid is driven off; cool and dilute to 200 cc. with water, add 20 cc. ethyl alcohol, allow to stand for 2 hours, filter on a Gooch crucible, wash with 1% sulfuric acid, ignite and weigh as lead sulfate. Calculate to lead with the factor 0.6829 or to the basic carbonate by 0.8526.

Carbonic Acid. A 1 gr. sample is placed in a flask containing a side arm delivery tube connected with a train consisting of two U-tubes containing sulfuric acid and potassium bichromate, two U-tubes containing soda-lime, and the fifth U-tube containing the same solution as the second sulfuric-bichromate tube. Add dilute nitric acid, and sweep out the liberated carbon dioxide with a current of air which has been freed from carbon dioxide by passing over soda-lime. Weigh the two soda-lime tubes, and the fifth tube, containing sulfuric acid-bichromate; the increase in weight is carbon dioxide.

Fineness. Treat as under litharge.

Sublimed White Lead.

Commercial sublimed white lead is a basic sulfate, containing, on an average, of about 78.5% of lead sulfate, 16% of lead oxide, and 5.5% of zinc oxide. It has a specific gravity of 6.20. It should pass through a 200 mesh screen without appreciable residue.

Sublimed white lead is used for its accelerating properties, which are almost entirely dependent upon the content of lead oxide. A test mix would undoubtedly be the best method for testing; the lead oxide may be calculated by determining the total sulfur and total lead, and after calculating the sulfur to lead sulfate the excess of lead may be calculated to lead oxide.

Sublimed Blue Lead.

Sublimed blue lead contains lead sulfate, sulfide, sulfite, oxide, and zinc oxide, with occasional traces of carbon. The fineness and accelerating properties are the only elements of interest; the specific gravity will be about 6.50 to 7.0.

Lead Oleate.

Lead oleate is a yellowish soft waxy solid, used to replace litharge because of the ease with which it may be distributed in a rubber mixing. The specific gravity is 1.50. It is claimed that

the lead oleate is much less harsh in its action than litharge, with less danger of burning the stock.

Magnesium Oxide.

Magnesium oxide, MgO, is sometimes called calcined magnesia from its method of preparation; it exerts a considerable influence on the vulcanization of rubber, although less than that of litharge. It is prepared by precipitation as the carbonate, and the latter ignited. It usually contains some calcium carbonate, but the amount must be kept very low in order not to interfere with its accelerating power. It has a specific gravity of from 3.20 to 3.45.

The calcium carbonate may be determined by solution of the sample in hydrochloric acid, and the separation of the calcium as oxalate from an ammoniacal solution, with ammonium oxalate. The calcium may then be determined in any desired way.

Because of its effect on the action of certain organic accelerators, magnesium oxide is sometimes used in amounts of 0.25% to 1.0%, in which case the accelerating effect of the magnesium oxide so used is small compared with that of the activated organic accelerator. As the principal, if not the only accelerator, it will be found in amounts up to 10%.

Magnesium Carbonate. Magnesium carbonate is a light, white powder, existing in a finer state of division than the oxide; its specific gravity is around 2.22. It may also contain calcium carbonate, which may be determined as under magnesium oxide.

The carbonate is not as powerful an accelerator as the oxide, and hence will be found in somewhat larger amounts; it is seldom used in less than amounts around 5%, and may go as high as 20%.

In the absence of any appreciable amounts of calcium, determine the magnesia content of the dry pigment by igniting to a dull red heat, to constant weight, taking care that the residue is cooled in a desiccator, and weighed in a stoppered weighing bottle, in order to prevent reabsorption of moisture.

Inorganic Fillers.

Aluminum Flake. Aluminum flake is essentially a mixture of hydrated aluminium oxide and silicate. It is a white powder,

with a specific gravity of from 2.58 to 2.65; with 2.60 as a fair average of the commercial lots. It contains very little moisture which may be driven off by heating at 100C. Continued ignition at a dull red heat shows an ignition loss of about 12%; the residue is the oxide and silicate. The ignited oxide is difficult to get into solution in hydrochloric acid, even when fused for a short time with sodium carbonate. This fact is important, both in the examination of the pigment, and in the analyses of ash.

On account of its low gravity and fineness, it is used to replace some of the zinc oxide in a compound, although it does not give as good tensile properties.

Ammonium Carbonate.

Commercial ammonium carbonate is a mixture of the carbonate and carbamate; it is used to supply the gas for making sponge rubbers.

Asbestine.

Asbestine is the trade name for a fairly pure magnesium silicate, specific gravity 2.60–2.80. It is used at times in place of talc for dusting stocks, and replaces whiting in some mixes. It is a cheap filling material.

Barytes.

Barium sulfate is used under various trade names, barytes, blanc fixe, basofor, barium dust, etc. Wiegand has shown that this pigment is a mere diluent; it is inert during vulcanization. On account of the crystalline nature of this pigment, it is not very well adapted for some lines of manufacture, but finds extensive use in mechanical goods. The specific gravity runs between 4.2 and 4.5. It should be free from grit and should leave no residue on a 200 mesh screen. Some preparations of barytes are claimed to have less than 1% of residue on a 300 mesh screen. The best means for telling the relative value of the various brands of barytes is by means of vulcanization tests with experimental batches.

Since barytes is used merely as a filler, it is seldom found in amounts under 10%, and there may be as high as 30% in the compound.

Brown Pigments.

The principal brown pigments are the various mixtures of iron and manganese oxides, the umbers. These are usually higher in manganese than the siennas. They should be tested for grit, and for change of color when heated.

Recent research has seemed to indicate that manganese is responsible for rapid deterioration of some rubber compounds; should this be substantiated with further work, it would seem to show that the manganese browns should be used with caution.

Calcium Sulfate.

Calcium sulfate is rarely used as such in rubber compounding, but it exists as a part of many lots of commercial golden and crimson sulfides of antimony.

Chinese Blue.

Blue is not a color which is used to any very great extent in rubber manufacture. The chief blues are Chinese blue, ultramarine blue, and the blue organic dyes.

Chinese (or Prussian) blue, is precipitated from a mixture of potassium ferrocyanide and ferric sulfate. It is an excellent blue color, but has limited possibilities in rubber, owing to its turning brown when mixed with alkalies, forming ferric oxide, and salts of hydrocyanic acid.

Crimson Antimony.

Crimson antimony is largely an oxide or oxysulfide of antimony, with a deep crimson, or red color; specific gravity varies from 3.9 to 4.2. It is usually lower in free sulfur than golden sulfide, and is used chiefly on account of its color.

Dyes.

The organic dyes are found chiefly in the sulfur chloride, or acid, cured goods. Practically none of them are water soluble, but most of them can be leached out with alcohol, acetone, or benzene. The identification of these dyes is an exceedingly diffi-

cult proposition; they are, as a rule, merely coloring materials, and have no other effect on the rubber, so that any dye which will give the same color is no doubt of equal value, and the positive identification of any one particular dye is not often a matter of interest.

Fossil Flour.

Fossil flour (tripoli, diatomaceous earth) consists of the remains of diatoms, and is nearly pure silica, with traces of alkali. It may contain considerable moisture, and the loss in weight at 105C is an important indication of its availability for rubber compounding. It is a very poor conductor of heat, and hence is frequently used in steam valves, etc. The specific gravity is about 2.00.

Gas Black.

Gas black is a very pure form of carbon, prepared by burning natural gas with insufficient air for complete combustion. It is the most finely divided pigment in use in rubber compounding; it contains no oil or grease, and on ignition leaves no residue. It has a specific gravity of 1.73, or less than one third of that of zinc oxide, so that a pound of gas black has more than three times the volume, and an even greater proportion of active surface. It is hygroscopic to a considerable degree, taking up moisture from the air to the extent of 2 or 3%.

Gas black should not be confused with lamp black, which is made from the burning of oils, tars, or resins, also with insufficient air for complete combustion. The flame may impinge on a revolving metallic cylinder, as in the case of gas black, or the oil may be fired in a huge oven, and the smoke carried through a series of chambers, thus making a partial separation of the different grades of black. Those nearest the fire are, of course, heavier, and contain a larger percentage of oil than the black contained in those chambers furthest away from the fire. These lamp blacks are further purified by heating, with the exclusion of air, thus reducing the percentage of oil. Lamp black is not as fine a pigment as gas black, and does not give the same improvement in tensile properties that the latter does; in fact, in this respect, it is rated below zinc oxide. It has the same specific gravity as gas black.

The only tests for gas black, or lamp black, are moisture, oils, and ash. Moisture should be determined on a 1 gr. sample by heating to 105C, cooling in a desiccator, and weighing in a stoppered weighing bottle. Oil is determined by extraction of a 5 gr. sample with ethyl ether, and weighing the residue. Not less than 5 gr. should be taken for the ash, and if the residue is an appreciable amount, it shows an admixture of other blacks, or dirt.

Owing to its low gravity, and fineness of particle size, gas black seldom runs higher than 10%, although there have been commercial articles manufactured containing 17–20%.

Golden Antimony.

Antimony sulfide, or golden sulfide, is a mixture of the tri- and penta-sulfides of antimony, free sulfur, and it may contain little or much calcium sulfate. The pigment varies from orange to a reddish color, the red being due to the oxide or oxysulfide. The composition varies within wide limits, as is shown by the variation in the specific gravity of from 2.5 to 2.9. It is not an accelerator of vulcanization; its real value consists in its ability to give up the free sulfur to rubber during vulcanization and yet, afterwards, to remain free from blooming. The free sulfur should run about 17%, and the calcium sulfate should be low. Caspari gives some figures showing that the free sulfur may vary from 7 to 19%; the calcium sulfate from 3 to 50%; and the antimony sulfides from 30 to 90%.

When used for coloring only, golden sulfide may be used only to the extent of 1 or 2%; when used as the source of sulfur for vulcanization, 15 to 25% will be required, depending largely upon the free sulfur and antimony sulfide content of the dry pigment.

Tests for Golden Sulfide.

Calcium sulfate. Jacobson [13] recommends the following simple test for calcium sulfate: Mix 1 gr. of the original sample with 2 gr. of sublimed ammonium sulfate in a porcelain crucible. Heat until the ammonium sulfate and antimony sulfide have been driven off; cool and weigh.

[13] Chem. Ztg. *32*, 984 (1908).

Free sulfur. Extract 1 gr. with acetone, or carbon bisulfide, in the extractor described under "acetone extract." Distil off the solvent, add 100 cc. of water and 3 to 5 cc. of bromine; proceed with the determination as directed under the determination of free sulfur in vulcanized articles. Or the solvent may be driven off in a tared flask, the flask and contents dried to constant weight at 90C, and the sulfur weighed directly. This method is shorter, but as a rule, not as accurate.[14]

Graphite.

Graphite, or plumbago, is a natural form of carbon, used to some extent on account of its lubricating value in preventing adhesion between rubber stocks and metal. It may be found in some stocks where its acid and alkali resisting properties are of peculiar value.

Greens.

Most of the green pigments used in rubber manufacture are organic colors. Brunswick green, a mixture of Chinese blue and chrome yellow (lead chromate), darkens when heated with sulfur. This green is sometimes marketed as "chrome green," but the true chrome green is the oxide of chromium, Cr_2O_3, and is by far the best mineral green for rubber work, since it is not readily affected by heat, acids, or alkalies.

[14] Luff and Porritt, J. Soc. Chem. Ind. *40,* 275-8T (1921), found by previously heating antimony sulfide before extracting the free sulfur, the latter varied considerably, as will be seen from the following table:

SULFUR EXTRACTED FROM ANTIMONY SULFIDE.
EXTRACTION FOR 5 HOURS WITH CARBON BISULFIDE.

	Unheated		Heated 1 to 2 hours		
Sample	1st 5 hours	2nd 5 hours	125 C	150 C	230 C
1	3.70	0.33	2.99	4.88	6.94
2	31.21	0.33	29.75	32.19	32.71
3	1.02	0.13	.95	1.01	.98
4	4.64	0.17	1.56	4.86	4.90
5	9.14	0.13	8.90	13.74	15.38

The presumption is that the sulfur extracted is available for vulcanization. If during vulcanization a greater percentage of free sulfur than that indicated at normal temperatures is available, this fact is of decided interest and value. It is desirable that this subject be followed up—we should know more definitely why at 125C the free sulfur drops off, and more particularly how long, after heating, the additional free sulfur is capable of being extracted with carbon bisulfide.

Iron Oxides.

Red oxide of iron (Indian red, Venetian red) is one of our most valuable pigments, not merely for its color, but for the valuable tensile properties which it imparts to rubber, ranking, in this respect, not very far behind zinc oxide. It is practically pure Fe_2O_3, running over 98%, with small amounts of water. It holds its color very well during vulcanization. The specific gravity is between 5.0 and 5.20.

These iron oxides may be obtained in a great variety of shades, depending largely on the method of preparation. The color should always be matched against a standard, and it is best to make a heat test at 150C, as recommended for golden sulfide.

Lime.

The lime which we use is the air slaked hydroxide, specific gravity of 2.4. It is used largely because it will take up small amounts of moisture which may be present in the compound, and reduce the danger of "blowing," or porosity. It has a decided hardening effect on the rubber, and hence may not be used in anything but small amounts. It also is believed to be responsible for rapid deterioration. It has some accelerating effect on the vulcanization, and due allowance must be made for this factor.

Lithopone.

Lithopone is a mixture of barium sulfate and zinc sulfide, containing about 25 to 30% of the latter. It is not as fine a pigment as the oxide, and does not produce as good tensile properties. It is unaltered during vulcanization, and is often used as a substitute for the more expensive zinc oxide. It must be low in water soluble matter, lead, and chlorides. The specific gravity is 4.20.

Tests for Lithopone.

Moisture. Heat 1 gr. for 2 hours at 105C, cool and weigh.

Barium Sulfate. To 1 gr. of pigment, add 10 cc. conc. hydrochloric acid and 1 gr. of potassium chlorate in small portions. Evaporate to half its volume, add 100 cc. of hot water, and a

few cc. of dilute sulfuric acid. Boil and filter, wash thoroughly, ignite and weigh the barium sulfate. Any silica, and some of the alumina, if present, would be included, but it is not worth attempting to make a separation.

Total zinc.[15] Take 1 gr. of the pigment, and boil with the following solution: Water 30 cc., ammonium chloride 4 grams, conc. hydrochloric acid 6 cc. Dilute to 200 cc. with hot water; add 2 cc. of a saturated solution of sodium thiosulfate, and titrate with a standard solution of potassium ferrocyanide, using 5% uranium nitrate as an outside indicator. Calculate the zinc to zinc sulfide.[16]

Fineness. Lithopone should leave practically no residue on a 200 mesh screen.

Sodium Bicarbonate.

Sodium bicarbonate is used in sponge rubber, since on heating it breaks down into the carbonate, carbon dioxide, and water. In the vulcanized article, it is found chiefly as the carbonate, Na_2CO_3.

Talc.

Talc is used extensively as a lubricant, to prevent rubber surfaces from sticking together, and in molds, to prevent the rubber stocks from sticking to the mold. It is rarely used as a filler, but rubber has such a facility for absorbing talc that the analyst will rarely fail to find 1% or 2% of talc in vulcanized compounds. The specific gravity is about 2.7, and the color will vary from a brilliant white to a dirty gray.

Talc usually has a considerable amount of grit, largely sand and the iron minerals which are usually found associated with talc (pyroxene, hornblende and biotite).

Ultramarine.

Ultramarine is probably a double silicate of sodium and aluminium, with some sodium sulfide. The sulfide seems an essential part; at least, if treated with acids, hydrogen sulfide is given off and the blue color fades out. It is the best known blue

[15] Low's Technical Methods of Ore Analysis, p. 284.

[16] There is a slight error here, owing to the fact that part of the zinc is present as the oxide, but the error is usually negligible.

pigment for hot vulcanization, but it is not safe to use it in goods for acid curing, since sulfur chloride usually contains free acid, and the latter would react with the ultramarine, and either partially or wholly destroy the color. The specific gravity is 2.35.

Vermilion.

The true vermilion is the sulfide of mercury, a very heavy pigment, specific gravity of about 8.00, but possessing a brilliant red color. It is the most expensive pigment used in commercial rubber goods, and since its color is its only good point, it is seldom worth what it costs, and is not likely to be encountered by the average analyst. Some so-called vermilions are merely red lakes. In the dry pigment, they are easily recognized by the difference in gravity.

Whiting.

On account of its low cost, whiting is extensively used. It is essentially calcium carbonate, and should be entirely soluble in dilute acids, and should contain no free alkali. It is somewhat hygroscopic, specific gravity 2.67, and contains small amounts of iron, alumina, and silica. It may be found in any amount up to say 25 or 30%.

Tests for Whiting.

Moisture. Heat 2 gr. for 2 hours at 105C; cool and weigh.

Free Alkali. In an Erlenmeyer flask, shake 10 gr. of pigment with 100 cc. of water, add a few drops of phenolphthalein; the color should not be deeper than a faint pink.

Water Soluble. Heat 10 gr. of pigment with 100 cc. of distilled water, filter, evaporate to dryness in a weighed beaker or dish, heat to 105C for 15 minutes, cool and weigh.

Fineness. Whiting should leave practically no residue on a 200 mesh screen.

Yellow Ochre.

The yellow ochres are practically all clays, containing large amounts of hydrated iron oxide; the specific gravity will vary enormously, probably more than any other pigment, from say 3.50 to 5.00. The higher gravity ochres are considered better

for the purpose; they hold their color better, have a stronger color, and are less likely to change color during vulcanization. The stronger colored ochres are to be preferred also, because less is required to give a definite color in the finished article.

Zinc Oxide.

Zinc oxide is unquestionably the most widely used pigment in rubber manufacture. Its extreme fineness makes it particularly valuable where strength and wear-resisting qualities are desired, it is unaffected in color during vulcanization, and hence can be used in any color combination. It has a special field of usefulness in that it also provides a rubber mix with an alkaline reaction, which permits many of the organic accelerators to function. Thiocarbanilide, the dithiocarbamates, thiurams, etc., will not accelerate vulcanization unless the mixture is basic, and zinc oxide answers the purpose in a most acceptable manner.

With some accelerators, zinc oxide reacts during vulcanization to form a new accelerator. The mechanism of such reactions is still a matter under investigation, and while splendid results have been accomplished by the workers in this field, we can hardly feel that the last word has been said on the subject. Probably the safest position to take is to say that practically all of the organic accelerators are more active in the presence of a basic oxide, such as magnesium, zinc and lead, and there are some which will not react without some such basic substance. In a few cases the marked difference between the reaction when zinc oxide is present, compared with some other basic oxide, suggests a possible reaction between the zinc oxide and the accelerator.

Zinc oxide may be absent altogether, it may constitute only a small percentage of the whole compound, or it may be as high as 50%, as for example, in some of the white tire treads.

Tests for Zinc Oxide.

Zinc oxide should be tested for moisture, lead, chlorides, sulfates, sulfides, and water-soluble matter. The specific gravity is 5.57, and the fineness such that there should be no residue on a 200 mesh screen, and very little on a 300 mesh. Over 0.1% of

lead renders it unfit for bright colored mixes, while much larger amounts would so change the vulcanization as to prevent its use altogether, unless, which seems unlikely, one could depend upon getting a zinc oxide with absolutely constant lead content. Chlorine is seldom found in amounts over 0.01, but cases have been known in which the chlorine ran over 0.20%. Such an amount will usually be reflected in an unusually high water soluble extract. Metallic chlorides have a deleterious effect on many rubber compounds, especially cements, and hence the chlorine content must be kept low.

Moisture. Dry 2 gr. at 105C for 2 hours, cool, weigh, and calculate the loss to percentage.

Insoluble Matter. In a 250 cc. beaker, treat 10 gr. with 50 cc. of conc. hydrochloric acid; evaporate to dryness, take up the residue with water and a few drops of hydrochloric acid, filter, and wash thoroughly with hot water. Ignite the residue, cool and weigh.

Water Soluble. Treat 10 gr. with 200 cc. of water, heat on a hot plate for one hour, filter into a 250 cc. graduated flask, cool to room temperature, and make up to the mark. Take a 50 cc. portion, evaporate to dryness in a weighed beaker or dish, dry for 2 hours at 105 C, cool and weigh.

Chlorides. From the water soluble extract take a 50 cc. portion, make slightly acid with nitric acid, add 10 cc. N/10 silver nitrate and a few drops of ferric chloride; titrate the excess of silver nitrate with standard ammonium thiocyanate.

Sulfates. To another 50 cc. portion of the soluble matter, add several drops of conc. hydrochloric acid, and heat; add 1 cc. of 10% barium chloride solution, allow to stand overnight; the next day, if there is any precipitate, it can be determined as usual.

Total Sulfur. Treat 10 gr. of pigment with 25 cc. of conc. hydrochloric acid and 10 cc. bromine water. Evaporate to dryness, take up with 50 cc. of hot water and a few drops of hydrochloric acid, filter from any insoluble matter; heat nearly to boiling, add 1 cc. of 10% barium chloride, and after standing overnight determine any barium sulfate which may have precipitated in the usual manner.

Lead. The filtrate from the determination of insoluble matter is nearly neutralized with sodium carbonate, and the lead pre-

cipitated with hydrogen sulfide. The qualitative test is usually sufficient; if desired, the lead sulfide may be determined by any of the usual methods.

Fineness. Place 10 gr. on a 200 mesh screen sieve, and, with a gentle current of water, wash the pigment through the screen. Any loose aggregates may be broken up with a policeman. There should be no residue. Repeat with a 300 mesh screen, and if anything remains on the screen, it should be transferred to filter paper, ignited, and weighed.

Chapter IV.

The Theory of Vulcanization.

Having before us the proposition that we are at this time primarily interested in the process of vulcanization as a change in chemical composition, without necessarily dealing with the manner in which such a change takes place, it seems as though a detailed study of the various theories of vulcanization is quite beyond the scope of the present work, and we will therefore go into the subject only to the extent necessary to develop the facts regarding the chemical changes during this process.

The term vulcanization has been used freely, and it will no doubt clarify matters if we attempt to define it.[1] For our purpose, we will assume that vulcanization will mean the addition of any element or group of elements, of which we may use sulfur and sulfur chloride as the principal examples, to crude rubber, or a mixture of crude rubber with other substances, whereby the crude rubber, or rubber mixing, is changed from a sticky, plastic mass into a substance having a certain degree of toughness, hardness, resiliency, and, in general, such properties as are usually associated with what we know as vulcanized rubber. By this definition, we purposely avoid including time or temperature

[1] It is of peculiar interest that while this book was in press an article by "Andrew H. King" appeared in Chem. & Met. Eng. 25, 1038-42 (1921), on "The Aging of Rubber," in which he gave a definition of vulcanization which so nearly parallels our own, as to make it well worth while quoting what he has to say:

"By vulcanization, we mean the addition of a substance or substances to rubber, which results in the production of a more elastic material, i.e., one with less plasticity. When the change becomes of a sufficient magnitude that the product becomes of commercial value, it is then known as 'cure.' It is well known that substances other than sulfur or sulfur chloride—for example, oxygen, chlorine, selenium, etc., produce a change in plasticity—in other words, they vulcanize—but the products obtained in this way have not to date had any commercial value, and therefore cannot be called 'cured.' In speaking of additional vulcanization, it is to be understood that we are not limiting ourselves to sulfur or sulfur chloride."

Later on, in the same article, "King" says: "A surface aging which results in hardening or checking of the surface, is probably due largely to additional vulcanization by oxygen;—internal aging may be sulfur and oxygen."

as a definite factor in the process; nor do we say that the process can, or cannot take place in the presence or absence of substances which may act as catalysts. The point which we wish to make regarding catalysts is, that they change the reaction as regards time, or temperature, or perhaps both, but they do not change the principal reaction itself. Taking the reaction between sulfur and crude rubber as an example, we finally come to the point where the rubber is saturated with sulfur, and has the formula $(C_{10}H_{16}S_2)_x$. By the use of catalysts, we would get exactly the same product, only in a shorter time, or at a lower temperature. The use of these catalysts is therefore a matter of commercial economy of time. It is true, when we use the longer processes, or higher temperatures, we have side reactions, depolymerization, etc., but the main process is the same in each case.

C. O. Weber found that when he heated rubber and sulfur together, he obtained a substance having as high as 32% of sulfur, corresponding to $(C_{10}H_{16}S_2)_x$; with sulfur chloride, he obtained $(C_{10}H_{16}S_2Cl_2)_x$. He therefore decided that rubber was a polyprene, and that it combined with sulfur to form a series of polyprene sulfides, the final product being identified as above. He was unable to isolate any of the intermediate products, and was obliged to assume their existence. Ostwald, reviewing the work of Weber, Höhn, Seeligmann, Axelrod, Hübener, Stern, Hinrichsen, and others, came to the conclusion that the chemical theory did not satisfactorily explain the matter, and that the facts as known were more in accordance with an adsorption process than a chemical one. He based his conclusions on the following: That there was always at least a small amount of free sulfur remaining after vulcanization (but which we now know is not so); that the process was a reversible one and that the rate of adsorption depended upon the amount of working which the rubber sustained. Special emphasis was laid on the temperature coefficient, 1.87, which seemed to agree more with the coefficient for an adsorption process than a chemical one. Ostwald was perhaps correct in saying that the evidence at the time was not sufficient to sustain the contention that the process was a chemical one; on the other hand, he himself included facts which as Loewen[2] has pointed out, are explainable only on the theory of a chemical process. In the preparation of the bromine and nitrosite deriva-

[2] Z. Angew. Chem. 25, 1553-60.

tives of rubber, it has been observed that the derivatives carry all of the combined sulfur, which would seem to indicate a chemical bond between the rubber and the sulfur. Spence showed that not only did the bromine derivatives carry all of the combined sulfur, but that in a series of compounds, the bromine and sulfur bore stoichiometric relations. Spence found evidence of an adsorption effect between the free sulfur and the rubber, preceding the actual chemical combination of the two. We shall see in due course, when taking up the subject of the direct determination of rubber, the importance of the conclusions which we reach regarding the nature of the reaction between rubber and sulfur.

Having arrived at the conclusion that the reaction is a chemical one, we may pass on to the mechanism of the reaction. Crude rubber will not combine with sulfur to any appreciable extent at ordinary temperatures. With the exception of what we have called the ultra-rapid accelerators (dithiocarbamates, etc.) there is no appreciable reaction until a temperature of at least 100C is obtained, and, for ordinary mixes, the rate at this temperature is exceedingly slow. The ordinary commercial range may be said to be between 125C and 150C. While exact data are lacking it has been estimated that for each 6 to 8C increase in temperature, the speed of the reaction is doubled, i.e., the time required for correct vulcanization is reduced by one half.[3] Furthermore, the speed of the reaction may be enormously altered by the addition of catalysts. It will be noted that the reaction takes place best when the mixture is weakly alkaline; acids, or strong alkalies, retard or even prevent the combination of rubber and sulfur. About 0.1% of caustic soda acts as an accelerating agent, 5% retards the reaction almost completely.

These accelerators not merely affect the speed, but also lower the temperature range at which appreciable vulcanization takes

[3] Probably every rubber chemist has some such formula on which he bases changes in curing, and while such figures are only approximate, they do give some idea of the order of magnitude of the change in the velocity of the reaction. The point is of particular commercial importance, because it shows the necessity for maintaining cures of rubber articles at exactly the prescribed time and temperature. For example, in a cure of 60 minutes at 140C, an error of 1C would be equivalent to adding from 8 to 10 minutes to the regular cure. Sufficient attention has not been paid to this important question, and the only reason that more trouble has not resulted is that the maximum in most compounds is not a point, but extends over a range of some minutes, and this automatically provides a certain tolerance. With rapid curing compounds, however, the maximum is usually just a point in the curve and a variation in the temperature results either in an under, or overcure.

place; some of them, as has been pointed out by Ostromuislenskii, Bruni, Bedford and others, increase the speed at ordinary temperatures to the point where it becomes noticeable.

One more noticeable action with these organic accelerators is the difference in the change in the velocity of the reaction, at ordinary temperatures, when the amount of the accelerator is varied. For example, 0.05% of the dimethyldithiocarbamate may be mixed with rubber, sulfur, and zinc oxide, at a temperature around 100C, for some time, without any noticeable effect on the rubber. With 0.25% of the same accelerator, in a few minutes a decided change takes place, and the rubber becomes hard and unworkable, and is clearly partially vulcanized.

Cold Vulcanization.

The acid cure process of cold vulcanization consists in submitting rubber to the action of sulfur monochloride, either in vapor form or in solution. The reaction is similar to that of hot vulcanization; the sulfur chloride adding at the double bond, forming an addition compound, but in this case, both sulfur and chlorine are added, and the resulting compound is different in chemical composition, although greatly resembling the hot vulcanization product in many of the tensile properties. One important fact stands out, that these properties are not as lasting in the acid cured as they are in the hot vulcanized rubber.

The reaction between rubber and sulfur chloride is practically instantaneous; consequently, an article to be manufactured by this method must first be brought to its final form prior to vulcanization. It has often been said that the reaction is a surface one, but this does not exactly explain the true state of affairs. In the case of a sheet of rubber exposed to the vapors of sulfur chloride, the gas will be absorbed by the outer surface, but before it can diffuse into the center of the sheet, chemical combination between the two takes place. This will continue until the surface has taken up all of the sulfur chloride with which it can combine. In the meantime, especially if the sheet is very thick, the center of the sheet is unchanged. A somewhat better distribution of the sulfur chloride is effected by swelling the sheet in solvents like benzene and then dipping the article in a solution of the sulfur

chloride in benzene. In this way, the penetration of the sulfur chloride is facilitated, and better results obtained.

There is no excess of sulfur chloride remaining as long as the rubber is at all unsaturated, and since there is no free sulfur, acid cured articles do not show the sulfur blooming so common with hot vulcanized articles.

Vulcanization With Mixed Gases.

A new method of cold vulcanization through the interaction of two gases, has been proposed by Peachey.[4] It consists simply in treating a rubber compound with sulfur dioxide, followed by hydrogen sulfide. Sulfur is liberated in such an active form that it can immediately combine with the rubber. In order to avoid the possibility of having sulfuric acid remain in the rubber, it has been found advantageous to use the sulfur dioxide first and follow this by an excess of hydrogen sulfide, since the latter is inert, and will, in time, be lost by diffusion. A control of the extent of the vulcanization is obtained by adding exact quantities of sulfur dioxide; since an excess of hydrogen sulfide is used, the exact amount of sulfur to be added to the rubber can be calculated.

Since this process of vulcanization takes place at ordinary temperatures, there is no doubt that, if practicable, it can be used with many substances as fillers which it is not possible to use under present conditions. This is especially true of some of the bright organic colors. It is very noticeable, for example, that a much wider range and more brilliant colors may be used with sulfur chloride vulcanization than with the hot vulcanization. It is, however, a question of time and temperature of heating; with the ultra-rapid accelerators, it is quite possible that this advantage will not be as marked as it is with the much slower accelerators.

[4] British patent 136,716, Feb. 21, 1921; cf. also Caoutchouc and Guttapercha *18*, 10744-5 (1921); Dubosc claims that in a discussion of the theory of vulcanization, he stated that the reaction may be caused by the production of colloidal sulfur. He showed that sulfur dioxide and hydrogen sulfide could be generated by the ingredients of a rubber compound, and further stated that if hydrogen sulfide and sulfur dioxide were simultaneously present, they would combine to liberate sulfur in such a form as to enable it to immediately combine with the rubber. In this instance, Dubosc was discussing the reaction in connection with the theory of hot vulcanization, but the latter was merely used as a source of the gases mentioned, and not necessarily the temperature at which the gases would unite to give off sulfur as indicated. Whether or not this may be called an anticipation of Peachey's patents remains to be decided.

Ostromuislenskii's Theories of Vulcanization.

Much has been said on the subject of the theories of vulcanization advanced by Ostromuislenskii, but if we can maintain our definition of vulcanization given in the beginning of this chapter, we cannot see that there exists any fundamental difference between his theories, and the present-day practice. He has shown that at ordinary temperatures, he can cause rubber and sulfur to unite in the presence of piperidyl-piperidine-dithiocarbamate. With a sufficient amount of accelerator, the same thing can be done with dimethyldithiocarbamate, but if we reduce the quantity of the accelerator to the neighborhood of 0.05%, then we will *find that the reaction will be so slow at ordinary temperatures as* to be commercially negligible. It now becomes merely a question of concentration of accelerator in order to make the velocity of the reaction at ordinary temperatures, which is so slow as to approach zero, approach a finite quantity that will be visible to the eye in a reasonably short time.

A much more distinctive process is the production of a vulcanized rubber substance by the addition of trinitrobenzene; with benzoyl peroxide, with halides and halide esters.[5] These products have some of the properties of rubber-sulfur vulcanizates. However, it must be concluded that we have here nothing to invalidate our present conception of vulcanization, and that what has been accomplished is to show that the change from the sticky, plastic rubber, which was first thought to be a function of sulfur, and was later extended to include sulfur chloride, is really a property of a number of substances. Some of these may require heating, and some do not; some require the presence of metallic oxides, and still others do not. As far as can be seen, the chief difference which has been noted up to this time, is the stability of the various products vulcanized in the different ways, and it may be that in order to arrive at a satisfactory definition of what we mean by vulcanization, we shall not only have to state that the vulcanized articles shall have certain definite properties,

[5] There is an excellent analogy here between the various combinations of rubber with elements, or groups of elements, and the similar reactions of the unsaturated fatty acids, such as linoleic, linolenic, etc. With sulfur and sulfur chloride, we have products quite similar to the addition product with oxygen, having many properties in common, such as solubility, etc.

but that the rate of decomposition, or deterioration, shall be not greater than a certain set figure.

To summarize the situation from the analyst's point of view: vulcanization is the chemical combination of rubber with other substances, without reference to time, temperature, catalysts (except as these remain as constituent parts of the mixture), or to any of the steps through which the products may have passed in reaching the final form in which the rubber is found. For example, there should be no chemical difference between rubber and sulfur which has combined as such and which has combined by reason of the treatment by Peachey's process.

Chapter V.

Sampling.

The sampling of rubber, and the materials to be used in the manufacture of rubber compounds, as is the case with a great many other commercial and natural materials, is usually done in the most casual fashion, whereas the proper sampling, and the care of the sample until the analysis has been completed, is fundamental. Unless the proper precautions are taken to make the sample represent the material from which it was taken, and maintain its condition and purity, not only is the accuracy of the analysis affected, but the incorrect results may frequently lead to false conclusions as to the manufacture or composition of the article. Samples for analysis have been packed, without adequate protection, in the same package with cans of oil; ground rubber samples in unsealed paper envelopes with bits of excelsior distributed throughout; inner tube samples which have been light checked; rubber articles with unmistakable evidence of having been placed against steam radiators; these do not appeal to the analyst as fertile fields for valuable results. Samples of less than 1 gr. may be very flattering to the ingenuity and ability of the receiver, but they can hardly be said to be representative of lots of finished goods weighing hundreds, or even thousands of pounds.

The process of sampling may be divided into three stages: (*a*) the taking of the sample; (*b*) its removal to the laboratory; (*c*) the preparation of the sample for analysis. The purpose of these three steps is to have the actual material used in making the various determinations of the same chemical composition as the lot which it represents. If the sample is to represent a number of pieces, the sample should be drawn to represent a fair average composition of the lot. More often it is not advisable to take more than one piece of a lot, or even a part of that. Under such conditions, we cannot speak of average composition, but since the supposition is that the entire lot is uniform, and that any one piece (or part of it), will truly represent, not the average, but the exact composition of all of the rest, in such cases we must

select our samples at random. Speaking generally, when we sample raw materials we should draw more than one sample, since these raw materials are apt to vary throughout the lot, and also because raw materials are thoroughly mixed in the process of manufacture, and it is the average composition which is of chief interest. With finished materials, the averaging process has already taken place, and it is a fair risk to assume that the lot is uniform.[1]

A. Taking the Sample. If the material is liquid, it should be thoroughly stirred before drawing off the sample. Particular attention should be taken to note whether there are two liquid layers, or whether there is any suspended matter (such as water in gasoline, or foots in vegetable oils). The liquid should be bottled at once, and sealed with a stopper which is not attacked by the liquid. The bottle should be scrupulously clean, both inside and outside, and should be dry.[2] Greases, waxes, and resins, are usually packed in small containers; a few ounces may be drawn from each container, or from a certain proportion of them. These small samples are united to form a composite sample, which is mixed and quartered until a final sample of about 100 to 200 gr. is obtained. This should be placed in a wide-mouthed bottle, or a can, and sealed.

Dry pigments are usually received in kegs or sacks. As in the case of greases, a small portion is withdrawn from some proportion of the containers; these are united, mixed and quartered, and a final sample of 100 to 200 gr. bottled and sealed.

The sampling of crude rubber is discussed in connection with the testing of crude rubber.[3]

B. Transportation to the Laboratory. The distance between the place where the sampling occurs, and that where it is to be tested, may be a matter of only a few feet, or it may be hundreds of miles. The principles involved are the same, irrespective of the

[1] This is particularly true in rubber goods, so far as actual composition is concerned; but such a sample will not reveal any variation in the vulcanization, since the latter process takes place in a relatively small number of units. We have met cases of rubber belting, for instance, which is vulcanized a portion at a time, where the manufacturer paid particular attention to the first and last part of the belt because that was where the samples would be taken. No amount of testing is proof against such chicanery.

[2] Samples of oil have been received, the container being an ink bottle in which a few drops of ink were still to be seen at the bottom of the bottle; and this sample was to be tested for mineral acids!

[3] Cf. page 22.

distance. The containers in which the raw materials are sent should be tightly stoppered, so as to avoid the introduction of dirt and other foreign matter, and also to prevent change in composition through evaporation or leakage.[4] Manufactured articles sent for analysis should be carefully wrapped.

The principal deteriorating agents of vulcanized rubber are heat, light, and oils. It is quite essential to see that each package is not only carefully wrapped, but that it will not come in contact with oils, and on packages which are to be sent any distance, specific instructions should be written on the outside, that such packages are to be kept in a clean, cool, dark and dry place. These same precautions should be observed in the laboratory, after the samples have been received.

If considerable stress has been laid on the care requisite for delivering the sample to the laboratory, our justification is that the analyst can test only what he receives; he cannot tell how great a change, or even at times that any change at all, has taken place. Questionable samples should be discarded at once; failure to do so will often lead to disagreeable controversies, which accomplish no good purpose, and tend to diminish that respect which the analyses of the laboratory should inspire.

C. Preparation of the Samples for Analysis.

Raw Materials. Pigments, oils, waxes, etc., should be mixed thoroughly before each portion is taken for analysis.

Unvulcanized Rubber Compounds. Sheet out rapidly on a cool mill, roll between holland and place in a covered can.

Reclaimed Rubber. Treat as under unvulcanized rubber compounds.

Cements. Cements should be stirred thoroughly before portions are taken for analysis, and then immediately covered. A fair sized quantity should be taken, the solvent removed, preferably by evaporation in thin layers at room temperature (if necessary, to remove the last traces of the solvent, the rubber may be heated for a short time between 80 and 90C, but it is better to avoid heating of any kind), and the residue sheeted out and rolled between holland, as in the case of other unvulcanized compounds.

[4] A sample of gasoline was sent to the laboratory in a can without a cover. It was delivered after working hours, and was not discovered until the next morning. Considerable evaporation had taken place, and the residue was hardly what it was expected to be.

Vulcanized Rubber Samples. Strip off all fabric, and see that the rubber is homogeneous, i.e., that there are not two or more compounds in the sample.

Grind about 50 gr. in a meat grinder, or coffee grinder, or by passing between the tightly closed rolls of a laboratory mill. Sift the ground material through a 20 mesh screen until about 25 gr. has been collected. It is not necessary to sift the entire amount of 50 gr.

The type of grinder is immaterial, providing the following precautions are observed: The sample must be ground at room temperature, without being appreciably heated up; no metal must be introduced into the sample during the grinding; and preference should be given to those grinders which tear the sample rather than just cut it up, since the former gives the greater surface for extraction.

Material containing fabric and rubber in such a manner as to make it impossible to produce good separation, shall be cut with scissors into as small pieces as is practicable. Rubber and fabric cannot be ground together, since segregation will be certain to occur on account of the difference in behavior on grinding, and this holds true even if the entire sample is ground and sifted.

Hard rubber samples are prepared for analysis by rasping.

Insulated wire should be cleaned with a damp cloth, to remove any adhering cotton or other adhering material, but care must be exerted to see that waxy hydrocarbons are not removed from the surface. If, however, a saturated braid sample must be used, remove the braid, and sandpaper the insulation for a depth of at least .005 in., and wipe with a damp cloth. This treatment will probably give low results for waxy hydrocarbons, and hence should be resorted to only when absolutely necessary, and a statement regarding the treatment given the sample should always be included as a part of the report of the analysis. On the other hand, it should always be indicated when analyses are made on samples which have been braided, or which have been vulcanized in contact with a saturated braid or tape, since there will be a migration of the liquid hydrocarbons of the saturation from the braid or tape, into the rubber insulation, and although the waxy hydrocarbons may be a bit low, because of the sandpapering of the surface, the acetone extract and the liquid hydrocarbons will be high.

Chapter VI.

Extractions.

Certain organic substances, mainly the oils and waxes, are removed by extract with acetone, chloroform, or by saponification with alcoholic potash. The results obtained by these three operations are largely qualitative, and from them may be obtained a fair index as to the quality of the article as a whole. In addition, there are some substances which may be determined quite accurately in these extracts.

Extraction Apparatus. The extraction apparatus should comply with the following requirements: It should be of the reflux type, with the condenser placed immediately above the cup which holds the sample; the sample must be suspended in the vapor of the boiling solvent; the cup must be of the syphon type; the cup must be far enough away from the sides of the extraction flask that it will be maintained at the temperature of the boiling point of the solvent; only glass or metal joints may be used—there shall be no cork, rubber, or similar material in the extractor, with which the solvent may come in contact, and from which extractable matter may be obtained.

The extraction flask may be of a size that will permit it to be weighed directly, or it is permissible to transfer the extract to a smaller flask for evaporation, drying, and weighing. The Cottle (better known as the Underwriters), the Joint Rubber Insulation Committee, and Bureau of Standards types are all satisfactory, and may be relied upon to give equally accurate results, but any extractor which fulfills the above requirements will do.

Acetone Extract.

The acetone used in this extraction must be redistilled, and free from water or acid. It should be distilled over sodium or potassium carbonate, and kept in clean dark-colored glass bottles.

Place 2.000 gr. of the sample in an acetone extracted paper

thimble, or fold it in an extracted filter paper; insert in the syphon cup, and extract continuously for eight hours.[1] The heating must be controlled so that the solvent syphons about 20 times per hour. Remove the solvent, dry the flask and contents at 90C to constant weight,[2] and calculate to percentage. This figure is usually called the "acetone extract, uncorrected." Due record should be made of the color and odor of the extract, and of any other peculiarities which may be noticeable. With high free sulfur, or waxy hydrocarbons, these substances will separate out on the sides of the flask.

Reserve the residue for the chloroform extraction.

The acetone dissolves the unchanged or free sulfur, vegetable fats or oils, rosin, mineral oils, paraffin, ceresin, ozokerite, a considerable portion of bituminous substances such as the mineral rubbers, tars, etc., and the so-called resins of the crude rubber. In simple mixtures, the separate constituents may be determined

[1] Eight hours should suffice for any properly prepared sample extracted under exact conditions. However, some uncured samples may fuse together into a solid mass, and require a longer time for comparatively complete extraction. In such cases, extract until the solution in the extraction cup is colorless, and continue for four hours longer. Uncured samples should be sheeted thin and rolled between hardened filter paper, to effect a thorough and more rapid extraction. The expression "complete extraction" is a misnomer: the free sulfur actually is extracted in the first four hours, but the soluble organic matter is extracted with difficulty. Additional quantities of extract can be dissolved up to 48 hours, or even more, but the amount so obtained is but a small proportion of the total, and is more or less constant. Hence, if we interrupt the extraction at a definite point, we secure results which serve the purpose of indicating the quality of the rubber, and are comparable with other extracts made in a similar manner. The same is true to a large extent with the chloroform and alcoholic potash extractions, and we really deal with comparable, rather than with absolute values.

The necessity for continuous extraction is explained on the same basis; with samples of approximately the same degree of fineness, the extraction is a matter of time, rather than the number of times the syphon empties; hence, standing overnight would permit the solvent to extract a considerable quantity of soluble matter that would not otherwise be extracted. Many of the variations in check results are really due to faulty manipulation, rather than to the type of extractor, or fineness of the sample.

[2] There has been considerable discussion as to the adoption of a standard time for drying. Some samples are dry in half an hour and it is a waste of time to continue for hours longer. On the other hand, the Joint Rubber Insulation Committee found some samples, notably those high in solid hydrocarbons, which were not dry in two hours. Sometimes in the hot, humid months of summer, water may condense on the outside of the condenser of the extractor, and some of this may find its way into the extraction flask. If it does, it must be removed, even if it does take more than half an hour; it is not extract, and must not be weighed as such. Of course, the longer periods for drying may lose a little more of the free sulfur than the shorter periods; especial care must be taken to see that the temperature does not go over 90C, for even at this temperature, there is some loss of free sulfur and at higher temperatures, over an extended period, the loss may be very great.

with some accuracy, but in the more complex ones only a few of the constituents may be determined with sufficient accuracy to be of any value. The free sulfur may always be determined with a high degree of accuracy; in the absence of tars and mineral rubber, paraffin and ceresin are capable of being determined with equal accuracy. Fatty oils will be associated with the rubber resins, and if we assume that the latter are about 3.5 to 4% of the rubber present, we may get a fair line on the quantity of vegetable oils, but such a scheme is only approximate.

Rosin may be determined by the method of E. J. Parry.[3] The fatty acids are dissolved in 20 cc. of 95% alcohol, a drop of phenolphthalein is added, and then strong caustic soda (one part of alkali to two parts of water) until the reaction is just alkaline. The solution is heated for a few minutes, allowed to cool, and then transferred to a 100 cc. stoppered graduated cylinder. The latter is filled to the mark with ether, 2 gr. of powdered silver nitrate is added, and the mixture shaken vigorously for fifteen minutes, in order to convert the acids into their silver salts. When the insoluble salts have settled, 50 cc. of the clear solution (containing the silver salts of rosin) is pipetted off into a second 100 cc. cylinder, and shaken with 20 cc. dilute hydrochloric acid (1 acid to 2 water). The ethereal layer is drawn off, and the aqueous layer is shaken twice with ether. The ether extracts are united, washed with water, and the ether distilled off in a weighed beaker. The residue, rosin, is dried at 110 to 115C, cooled, and weighed.

This is an excellent means of separating fatty oils and rosin; it is best performed by taking the water solution in the determination of unsaponifiable matter, making it acid with hydrochloric acid, and extracting the liberated fatty acids with ether. The ether must be driven off, and the fatty acids dried, before the method may be used.

The mineral oils can be partly separated from hard paraffin, sufficiently so as to give some indication of the composition. So far as our experience goes, no method has been given which will determine the relative amounts of mineral rubber and paraffin in a mixture of the two. The possibilities of such a method being developed are very remote, in view of the wide variations in

[3] Allen's Commercial Organic Analysis, 4th ed., Vol. V, p. 73.

the composition of the mineral rubbers, and the fact that chemically they are so nearly like paraffin.

Chloroform Extract.

The chloroform extraction is performed in the same apparatus used in making the acetone extraction. The chloroform should be redistilled over alkali.

Extract for four hours, the residue from the acetone extraction (it is not necessary to remove the acetone adhering to the sample), using about 60 cc. of the solvent. If at the end of four hours, the solvent in the syphon cup is still colored, continue to extract until it is colorless. Filter the extract through fat free filter paper into a small Erlenmeyer flask, distil off the solvent, and dry the flask and contents to constant weight at 95C.

If the chloroform extraction cannot be started immediately after the acetone extraction has been completed, the sample should be protected against oxidation by keeping it in a vacuum desiccator in a vacuum of at least 50 mm of mercury. Vulcanized rubber which has been extracted with acetone oxidizes very rapidly in the air and the resultant products are so soluble in chloroform as to yield hopelessly false results, being as much as five to ten times the true amount.

Reserve the residue from the chloroform extraction for treatment with alcoholic potash.

The chloroform dissolves part of the rubber, particularly the undercured, and the oxidized rubber. Its chief value is that it dissolves part of the mineral rubber, the solution taking on an intense brown or black color. It is an invaluable qualitative test for mineral rubbers, the color being quite distinctive, and not likely to be mistaken for anything else.

The chloroform extract in a well cured and unoxidized sample of soft vulcanized rubber, will run from 1 to 3% of the rubber present, with the average nearer the lower figure. It has been suggested as means of determining whether or not the rubber has been undercured, but the data available are largely limited to insulation compounds, and are not entirely convincing.

Alcoholic Potash Extract.

Dry the residue from the chloroform extraction at 60C until the odor of chloroform is no longer noticeable. Place the rubber

in a 200 cc. Erlenmeyer flask, and cover with 50 cc. normal alcoholic potash.[4] Boil for four hours under reflux condenser. Filter by decantation through a hardened filter paper, wash with two portions of 25 cc. of hot alcohol, and then thoroughly with hot water. Evaporate the filtrate to dryness, take up in warm water and when the solution has been effected, cool to room temperature. Transfer to a separatory funnel, add 30 cc. N/5 hydrochloric acid and sufficient water to bring the total up to about 100 cc. Add 40 cc. of ethyl ether, shake thoroughly, allow to stand until the two layers are completely separated, draw off the water into a second separatory funnel, and continue to extract with 20 cc. portions of ether until a colorless solution results, and then twice more. Unite all the ether fractions in the first separatory funnel, and wash with water until the water shows no further acidity (test with silver nitrate solution). Filter the ether through a plug of extracted cotton into a weighed beaker or flask, evaporate to dryness, and dry to constant weight at 95C.

Another method for the determination of the alcoholic potash extract is to dry the residue from the chloroform extract, cool, and weigh. Place the rubber residue in a 200 cc. Erlenmeyer flask, add 50 cc. N/1 alcoholic potash, and boil under a reflux condenser for four hours. Filter off the rubber on a Gooch or alundum crucible, wash with hot alcohol, and then hot water, until the washings are free from alkali; dry in an inert atmosphere to constant weight; the loss in weight is the oil substitute.[5]

[4] We should not be led astray by those who wish to replace potassium hydroxide with sodium hydroxide. When the former was difficult to obtain, one did what could be done with the material which was available, but no question of a slightly higher cost should interfere now with the use of a better and more widely known reagent. On the other hand, with pure grain alcohol difficult to obtain under present conditions in the United States, the use of methylated alcohol becomes almost obligatory. It is hard to see just what error would be introduced by the presence of methyl alcohol; it is difficult to conceive of anything which might be present in a rubber compound which is soluble in methyl alcohol, and insoluble in acetone, chloroform or ethyl alcohol. If the analyst will see that his denatured alcohol has been denatured with methyl alcohol, and will use this denatured alcohol only after redistillation over caustic potash, the chances for error are very small indeed. Of course, in any event, and regardless of the kind of alcohol used, a blank is always run, and due correction made for the results found. Again, no careful analyst will use an alcoholic potash solution which has been standing a long time, and particularly if it is badly discolored.

[5] This method is not as accurate as the previously mentioned one, and is not to be recommended. There is the greatest difficulty in washing out all of the alkali, and the latter cannot be removed with acids on account of the probability of these acids attacking some of the pigments in the rubber.

Ordinary crude rubber shows a small amount of material soluble in alcoholic potash, usually around 1% of the amount of rubber. This will be included in the results in either method. In the first method, we weigh the fatty acids, although they were present originally as the glycerides; i.e., we weigh only 95% of the substitute. These two elements tend to neutralize each other, and the result is a pretty accurate determination of the amount of fatty substitute, not including, of course, any unchanged oil which would have been extracted in acetone, or any pigments contained in the substitute.

If vegetable oils are used, and there is sufficient sulfur present, we may find that a part of the oil has been converted into an insoluble form, and will appear at this point. There is no way to distinguish substitute formed during vulcanization and that added as such, excepting that the oil in the substitute is usually very well changed into the acetone-insoluble form, whereas the oil added as such will be changed to only a slight extent.

The method involving loss of weight is practically worthless, because it is an almost hopeless task to thoroughly wash out the alkali. In one case continuous washing for 8 hours did not suffice, and acid cannot be used to neutralize the alkali, on account of its effect on the acid-soluble fillers.

Analysis of Acetone Extract.

Unsaponifiable Matter.

Add to the acetone extract, 50 cc. of alcoholic potash, boil under a reflux condenser for two hours, and evaporate to dryness. Add 10 cc. of water and 20 cc. of ether, heat until solution is complete; cool, and transfer to a separatory funnel, wash out with warm water, and cool, then with two 20 cc. portions of ether; the separatory funnel should contain 100 cc. of water, and not less than 40 cc. of ether. Shake vigorously, allow the two layers to separate, and draw off the aqueous layer into a second separatory funnel. Repeat the extraction until no further material can be extracted (not less than four extractions should be made). Unite the ether portions of the extract, and wash with water until free from alkali (the first two portions may be united with the original aqueous solution, and the whole reserved for the determination of free sulfur). Filter the ethereal layer through extracted cotton, wash-

ing with ether and hot chloroform, using the latter to rinse the original flask, and both separatory funnels. Evaporate to dryness, dry to constant weight at 95 to 100C, cool and weigh.

The above method gives the liquid and solid hydrocarbons, and the unsaponifiable resins. The difference between the total extract, and the sum of the free sulfur and unsaponifiable matter, will consist of the saponifiable resins, and any fatty oils which may have been extracted. The acetone soluble matter of the mineral rubber will be found largely in the unsaponifiable portion. Rosin, as its composition indicates, will be distributed between the two, about 90% being saponifiable.

Waxy Hydrocarbons.

The time-honored method for separating the solid paraffins has been to dissolve the unsaponifiable portion in alcohol, and freeze out the paraffin. However, some of the latter will always remain in the alcohol, along with any liquid mineral oils, and the unsaponifiable rubber resins. The Joint Rubber Insulation Committee devised a method for correcting for the alcohol soluble paraffin, in the absence of mineral oils, or, if the latter were present, to get the total soluble paraffins and the mineral oil together. The alcohol insoluble paraffins are called "Waxy hydrocarbons A" and the soluble paraffins are called "Waxy hydrocarbons B." If the latter are solid, the sum of the two is the total paraffin in the sample.

If it is desired to know only the total mineral hydrocarbons, then the method for Waxy hydrocarbons B is used directly.

Waxy Hydrocarbons A.

Add 50 cc. absolute alcohol to the unsaponifiable matter and warm until solution is as complete as possible. Cool the solution to —4 or —5C, and maintain at this temperature, or lower, by packing the flask in a mixture of ice and salt. Filter out the waxy hydrocarbons, using a funnel packed with ice and salt and applying suction if necessary. Wash the flask and filter with 25 cc. of 95% alcohol which has been previously cooled to the same temperature. Dissolve the residue on the filter paper in hot chloroform into the original flask; evaporate the chloroform, and dry the residue at 95 to 100C to constant weight.

Waxy Hydrocarbons B.

Evaporate the alcohol from the determination of Waxy hydrocarbons A, add 25 cc. of carbon tetrachloride, and transfer to a separatory funnel. Shake with conc. sulfuric acid, drain off the discolored acid, and repeat with fresh portions of the acid until there is no longer any discoloration. Vigorous shaking is absolutely necessary for the success of the method. After drawing off all of the acid, wash the carbon tetrachloride solution with repeated portions of water until all traces of acid are removed.[6] Transfer the carbon tetrachloride solution to a weighed flask, evaporate off the solvent, and dry to constant weight at 95 to 100C. Note whether the residue is solid, liquid, or pasty.

[6] On account of the specific gravity of the carbon tetrachloride washing with water is a very tedious proposition, because the carbon tetrachloride must be drawn off with each washing, and returned to the flask. While the Joint Rubber Insulation Committee did not recommend it, the carbon tetrachloride may be diluted with ether until the mixed solvents have a gravity lower than that of water; the washing can then be continued as usual with separatory funnel washings. Ether to the extent of about two and a half to three times the volume of carbon tetrachloride will be necessary to have the ether-tetrachloride mixture float on the water layer.

Chapter VII.

The Determination of Rubber.

It is a peculiar fact concerning the analysis of rubber that the determination of the principal constituent involved is seldom, if ever, made by a direct determination. A tremendous amount of research has been undertaken, methods and revisions of methods have been suggested, but as yet no one method has succeeded in securing the endorsement of the rubber analysts.

The methods for the determination of rubber may be classified under three headings: (1) direct; (2) indirect; (3) difference. In No. 1, the idea is to form a definite compound with rubber and either weigh the compound directly or determine some part of the compound and from these figures, to calculate the total rubber. The two principal methods in this group are the tetrabromide methods and the nitrosite methods. The indirect methods (No. 2), proceed to separate the rubber, but the latter is not determined as such, but is determined as the loss during the solution. The difference methods comprise the third group, and the principle involved is merely to determine every other known constituent, subtract the total from 100%, and call the remainder rubber.

The Tetrabromide Method.

The tetrabromide method was first advocated by Budde, for use in determining the rubber in unvulcanized compounds, or crude rubber. The bromination solution used was 6 gr. of bromide and 1 gr. of iodine in 1000 cc. of carbon tetrachloride. The rubber was swollen in carbon tetrachloride, and filtered. The clear solution was treated with 50 cc. of the bromine solution, allowed to stand for 24 hours, diluted with an equal volume of alcohol, and when the precipitate had settled it was filtered and washed with carbon tetrachloride-alcohol (1-1), and finally, to remove the bromine, with alcohol. The precipitate was weighed as $C_{10}H_{16}Br_4$, and calculated to rubber, using the factor 0.298.

The gravimetric method did not prove successful, and evoked considerable criticism. Fendler, Harries, Hubener, Spence, and others, presented various modifications, and, in the meanwhile, Budde had published a volumetric method, which he claimed was satisfactory for rubber vulcanized with sulfur chloride. In this method, the rubber swollen in carbon tetrachloride was treated with the brominating mixture, and after the tetrabromide had been filtered free from bromine, it was treated with conc. nitric acid and N/5 silver nitrate, and the bromine determined as in Volhard's method.

The volumetric method did not prove any more acceptable than the gravimetric. For some compounds, good results were obtained, but in others, especially with vulcanized rubber, it was found that the bromine did not replace the sulfur of vulcanization. There was also found to be a loss of bromine during the acid treatment, which Spence corrected by fusing the tetrabromide with alkali. Vulcanized samples gave low results, but when it was noted that the sulfur combined with the double bonds of rubber in stoichiometric proportions, it was seen that by adding to the bromine found in the tetrabromide the bromine equivalent of the sulfur of vulcanization ($2Br = S$), the results were more uniform, and more nearly correct. It was also noticed that hydrobromic acid was formed during bromination, and efforts were made to eliminate this factor by freezing the brominating solution, but, on the whole, while cooling reduced the formation of hydrobromic acid, it did not eliminate it.

Recently, further attempts have been made to make the method practical. Lewis and McAdam[1] published a modification based on McIlhenny's[2] method for the determination of substitution, and Fisher, Gray and Merling[3] have recommended some improvements in the Lewis and McAdam method.

When bromine adds to rubber, whether the latter be vulcanized or not, there are a number of ways in which the reaction may progress:

(1) $HC : CH + 2\,Br = HCBr.HCBr$
(2) $HCBr.HCBr = HC : CBr + HBr$
(3) $HC : CBr + 2\,Br = HCBr.CBr_2$
(4) $HC : CH + HBr = HCBr.CH_2$
(5) $CH_2.CH_2 + Br_2 = CHBr.CH_2 + HBr$

[1] J. Ind. Eng. Chem. *12*, 675-6 (1920).
[2] J. Am. Chem. Soc. *21*, 1084 (1899).
[3] J. Ind. Eng. Chem. *13*, 1031-4 (1921).

The first reaction is purely additive; the second is a splitting off of HBr, re-forming the double bond, which again combines with 2 Br as shown in No. 3; the liberated hydrobromic acid may unite at a new double bond, as in No. 4; and finally, No. 5 is a case of straight substitution. The resulting product will contain HCBr.HCBr; $HCBr.CH_2$; $HCBr.CBr_2$; HBr and Br. It is apparent that every molecule of HBr remaining uncombined with the rubber represents a loss of 2 Br from the excess over that required for the double bonds. This has been one of the serious errors, and it is one which varies greatly with variations in the condition of time, temperature, and concentration of the solutions.

In determining the iodine number of "burnt" linseed oils, Smith and Tuttle [4] found that concordant results could be obtained only when a very exact procedure was followed, in which the weight of the sample, volume and strength of the iodine solution, time and temperature of the reaction, were specified within very narrow tolerances. The analogy in chemical reaction between drying oils and rubber, is very striking, and we may expect to find just as great difficulties with vulcanized rubber as with oxidized linseed oil. Lewis and McAdam brominate for 2-4 hours, while Fisher, Gray and Merling say 2.5 to 3.5 hours. The amount of the sample is quite indefinite, not over 2.00 gr. for unvulcanized; 1.50 to 2.00 gr. for vulcanized. In the latter case, no special attention seems to have been paid to whether the material contained 30 or 90% of rubber hydrocarbons; nor to whether they are dealing with rubber having a vulcanization coefficient of 2.0 or 10.0. There is a considerable amount of lack of definiteness in a reaction which, in a similar determination (adding halogen to partly oxidized oils), has been shown to be absolutely essential. It is perhaps not to be wondered at that after so many years of trial, there still remains such an element of doubt.

In spite of the fact that it requires an extra determination (sulfur of vulcanization), the tetrabromide method offers an excellent opportunity for a direct method, if some one will take the time to ascertain the exact conditions which are necessary for consistent results.

[4] J. Ind. and Eng. Chem. 6, 994 (1914).

Nitrosite Method.

The nitrosite method was first described by Harries.[5] He found that by allowing N_2O_3 to react for a sufficient time with a solution of rubber, he obtained a final product of constant composition, $C_{10}H_{15}N_3O_7$, and by weighing this material, the rubber hydrocarbon could be calculated. Rubber resins were removed by extraction with acetone. Alexander in attempting to repeat Harries work, claimed that during the formation of the nitrosite, carbon dioxide was given off, and that the composition of the final nitrosite of Harries was really $C_9H_{12}N_2O_6$. The loss of carbon dioxide has not been confirmed by any other workers in this field, so that if carbon dioxide was really lost, as Alexander says, it was because of some condition not in accordance with Harries method. However that may be, every one agreed upon the difficulty in getting a constant composition for their end product, and this method was more or less abandoned until Wesson[6] took it up from a new angle. He proved that Alexander was wrong in his statement that carbon dioxide was lost, and hence, although the final product varied in composition, it still held all of its original carbon. If, therefore, the carbon in the nitrosite was determined, a simple calculation could be made directly to rubber which did not depend upon any definite composition of the nitrosite and was independent of the sulfur of vulcanization. Wesson secured some good results on a few compounds, but with some complicated commercial compounds, large differences cropped out. Tuttle and Yurow,[7] while investigating the possibilities of Wesson's method, found that his best results were obtained by a fortunate balancing of errors, and that when the causes for these errors were removed, accurate results could be obtained directly in the presence of practically any known organic or inorganic fillers. The only unfortunate circumstance connected with this method is the fact that it requires a fairly complicated combustion train, and this has prevented many laboratories from testing it out. Perhaps further experimentation along the lines of wet combustion would simplify it sufficiently to permit its more general adoption. In the meantime, it stands as

[5] Ber. *34*, 2991-2 (1901); *35*, 3256: 4429 (1902); *36*, 1937 (1903).
[6] J. Ind. Eng. Chem. 5, 398 (1913); *6*, 459-62 (1914); *9*, 139-40 (1917).
[7] India Rubber World, *57*, 17-8 (1917); Bureau of Standards Technologic Paper 145 (1919).

our only accurate direct method for the determination of rubber irrespective of the condition of the rubber product, and the degree of vulcanization. The method is as follows:

The preliminary extractions with acetone, chloroform, and alcoholic potash will show whether mineral rubbers or oil substitutes are present. If the former, then acetone and chloroform extractions are necessary; and with oil substitutes, make acetone and alcoholic potash extractions; and if both are present, make all three extractions. When an alcoholic potash extraction is made, wash the sample thoroughly with 5% hydrochloric acid hot water and alcohol.

Take 0.500 gr. of the finely ground sample (call this weight W), and extract with acetone for eight hours (make other extractions, if necessary, as stated above). Dry the residue in hydrogen (or other inert gas) for two hours at 100C. Place the sample in 50 to 75 cc. of chloroform and allow it to swell. Pass into this until the green color which is formed persists for 30 minutes, the gases formed by heating arsenic trioxide and nitric acid of specific gravity 1.30. To avoid contamination, it is important that no rubber connections be used. Immerse the flask containing the rubber in cold water during the nitration. Allow the solution to stand overnight; the next day, filter off the nitrosite through a Gooch crucible and wash with small quantities of chloroform. Remove the acid gases and chloroform from the flask by means of a gentle current of air. Evaporate the filtrate to dryness. Dissolve the nitrosite remaining in the flask in the Gooch crucible and in the residue from the filtrate in acetone and filter the solution through asbestos into a weight-burette The total volume should be about 100 cc. Allow this solution to stand for a short time to permit any sediment which may form to settle out in the bottom of the weight burette.[8] Weigh the burette before and after filling, calling the difference N. Draw off about 25 cc. into a small Erlenmeyer flask, reweigh the burette, and call the difference O. Evaporate the portion drawn off to a small volume, transfer to a porcelain boat (about 14 cm long and 1 cm. wide), which has been filled with alundum, and wash the flask with acetone (it is best to make this transfer in small portions, drying the boat and contents for a few minutes be-

[8] The usual type of weight burette will not answer; it is necessary to have the solution drawn off at the side, about an inch from the bottom. See B. of S. Tech. Paper 145 for a sketch of the weight burette.

tween each addition). After the final washing and drying, add 1 or 2 cc. of 1% solution of ammonia in distilled water,[9] and dry in an inert gas for one hour at 90C. Repeat with a second portion of ammonia and dry as before. By this means, all of the organic solvent will be removed.

Place the boat in the furnace, and proceed with the combustion. Pass the products of combustion through U-tubes or other satisfactory absorption tubes, placed in the following order: a, b, c, potassium bichromate-conc. sulfuric acid; d, 20-mesh powdered zinc; e, f, soda-lime and calcium chloride; g, potassium bichromate-conc. sulfuric acid; h, dilute palladium chloride solution, (very little palladium chloride is needed; use about a drop of a 10% solution in 10 cc. of water). Weigh e, f, and g before and after each combustion; refill c and g frequently from the same stock solution, so that the gases which enter e, and those that leave g, will have the same moisture content. The palladium chloride serves to detect the presence of carbon monoxide or other reducing gases; if there is any blackening, it shows incomplete oxidation, and, in this event, the results must be discarded and the determination repeated.

The carbon dioxide will equal the algebraic sum of the differences in tubes e, f, and g. Call this sum P. The factor for calculating from carbon dioxide to rubber hydrocarbons, is .309. The formula is therefore as follows:

$$\frac{P \times 0.309 \times N \times 100}{O \times W} = \% \text{ of rubber hydrocarbons.}$$

Correct this figure for whatever extractions were made previous to nitration.[10]

The Indirect Methods.

The indirect methods comprise those in which the rubber is decomposed and rendered soluble in some solvent, and the material which goes into solution is called rubber hydrocarbons. A great many solvents have been suggested, heavy petroleum (B.P. 230-280), anisole, phenetole, xylol, paraffin oil, camphor oil, tere-

[9] The nitrosite precipitate is insoluble in distilled water, and in acids; it is soluble in aqueous alkaline solutions. Ammonium hydroxide is used simply because it provides the necessary alkalinity, is volatile, and, even if it is not completely driven off, introduces no error whatsoever.

[10] In case the extractions contain other material than rubber, the correction applied must be an arbitrary one. It will be recalled that the true resin content of high grade rubber is about 4% or less, and the normal chloroform and alcoholic potash extracts of rubber are about 2% and 1% respectively.

bene, turpentine, salol, nitrobenzene, aniline, cumene and cymene. The general procedure is the same for all of them; the acetone, chloroform and alcoholic potash extractions remove the soluble organic fillers; the solvent is then added and heated until the rubber passes into solution. The fillers are separated by filtration and weighed, and the loss is vulcanized rubber. Sometimes special steps are taken to bring the fillers into a state in which they can be easily filtered. All sorts of solvents are used to wash the fillers.

The principal objection to these methods is that one can never be sure that there are no organic or inorganic fillers passing into solution, or that insoluble organic compounds are not formed from the rubber and solvent. Correction after correction must be applied, until finally, instead of a determination of rubber, we have almost a complete system of analysis.

Difference Methods.

There is really no sharp line dividing the difference methods from the indirect methods, but we have reserved the term "difference" methods for those which remove the rubber by ignition. Such methods are widely used, largely because they are rapid, and it is a fact that they are frequently quite accurate, especially in the absence of organic fillers. In most cases, the sample is subjected to acetone, chloroform and alcoholic potash extractions, and then ignited. At times, only the acetone extraction is made. A more complicated, and more exact procedure, is that of the Joint Rubber Insulation Committee.[11] This method is intended for 30% and 40% insulation compounds, but may be used for any compound containing no organic fillers. Mineral rubber, lampblack, glue, cellulose, etc., all give high results. The method is as follows:

Add to the rubber residue from the alcoholic potash extraction, sufficient water to make the total volume 125 cc., and then add 25 cc. conc. hydrochloric acid. Heat for one hour, decant through a Buchener funnel, using hardened paper, and wash with 25 cc. of hot water; repeat this treat twice. The rubber should be white, and free from black specks from undissolved fillers (lead sulfide). Wash the rubber free from chlorides, transfer the rubber to the filter paper, dry as much as possible by suction,

[11] Am. Inst. Elec. Eng., April, 1917.

wash with 50 cc. of 95% alcohol, and transfer the entire residue to a weighing bottle. Dry to constant weight at 95 to 100C. Let this weight be represented by C.

On a portion D of this residue C, determine the ash E (see below) and the sulfur F in ash E. Determine the sulfur H in another portion G of residue C.

To determine E, place about 0.50 of residue C into a weighed porcelain crucible, heat gradually until the crucible has ceased to smoke, then raise the temperature and heat until all organic matter is destroyed. Cool and weigh, calling the residue E. If E is small, the determination of sulfur in the ash may be omitted, and F assumed to be zero. From the data thus obtained, the percentage of rubber hydrocarbons in the original material is calculated as follows:

$$\frac{100\ C}{4}\left(1 - \frac{E - F}{D} - \frac{H}{G}\right) = \%\ \text{rubber hydrocarbons.}$$

The simplest method of all, is the determination of the ash. Wrap a 1 gr. sample in filter paper, and extract with acetone for four hours; ignite the residue in a porcelain crucible; cool and weigh. Correct for the sulfur in the ash by adding a few drops of nitric acid-bromine mixture, heat on the steambath, then add 5 gr. sodium carbonate, dry carefully until all moisture is removed, fuse the residue, extract with hot water and filter; make the filtrate just acid with hydrochloric acid, heat to boiling, add barium chloride solution, and determine the barium sulfate as usual. Deduct the sulfur thus found from the residue on ignition, and the difference is called "ash, sulfur free."

In the ash method, rubber is the difference between 100% and the sum of the total sulfur, ash (sulfur free), and any other determinations of fillers which may have been made.

The only good word which can be said for the ash determination as a correct method for the determination of rubber, is that it requires only a crucible, a Bunsen burner, and a balance.[12]

[12] It is quite within reason that those analysts who have for years been adhering to the "ash method," will find fault with this statement. With a few simple compounds, satisfactory results may be obtained, but beyond this nothing is certain. Our experience with this method, in testing rubber materials for the U. S. Government over a number of years, demonstrated only too clearly how easy it was to be led astray by results obtained with the ash method. The errors in this ash method are frequently very large—it is only the occasional determination which comes with 2 or 3% of the truth. The plain truth of the matter is that the ash method is used because it involves little labor, and requires but a short time to complete, but if a reasonable degree of accuracy is not necessary, one is tempted to ask "Why make the determination at all?"

Chapter VIII.

Sulfur Determinations.

Total Sulfur.

Sulfur may occur in rubber compounds in any of the following forms:

(*a*) Free sulfur.
(*b*) Sulfur combined with the rubber.
(*c*) Sulfur in organic compounds (mineral rubber, oil substitutes, accelerators).
(*d*) Sulfides (zinc, antimony, mercury, lead, cadmium).
(*e*) Sulfites and sulfates (calcium, barium, lead).

In addition to the above, there are other substances, such as barium carbonate, lead oxide, etc., which, while not containing sulfur, are important factors in deciding what method is satisfactory for the determination of sulfur. We may say that all rubber compounds will contain classes (*a*) and (*b*), but beyond that, nothing definite may be assumed. It is obvious that if many of these sulfur-bearing substances are present, the determination of total sulfur becomes a difficult proposition, and, moreover, the results obtained decrease in value.

In looking over the foregoing list, it is obvious that three steps are essential: (1) oxidation of organic and inorganic substances; (2) fusion of inorganic substances; (3) separation of metals forming insoluble sulphates by filtration of the alkaline solution of the fusion.

The purpose of the oxidation is obvious; the oxidizing agent must be sufficiently effective to oxidize rather large amounts of free sulfur (frequently 5%, and possibly 10% or 12%). Since it is assumed that oxidation will be accompanied or followed by fusion, it is not essential that the oxidizing treatment be carried to the point of the complete oxidation of all of the organic substances. The period of fusion must suffice to convert insoluble

into soluble sulfates. These steps are fairly well agreed upon, although various means are suggested for this part of the procedure. The third step, filtration, is still a subject of controversy, although why it should be so is difficult to understand. If the solution is acidified before filtration, we may expect to form calcium, lead, and barium sulfates. Calcium sulfate is highly soluble, lead appreciably so, and barium sulfate scarcely at all. Calcium may have been present originally as the carbonate (whiting), or as the sulphate (in antimony compounds); the lead as oxide, sulfide, sulfite, or sulfate, and barium as the carbonate or sulfate. The purpose of the filtration from an acid solution is to thus eliminate the insoluble sulfates originally present in the rubber mixture, but this will be accomplished only when barium sulfate is the only sulfate originally present, and lead and calcium are present in very small amounts, and barium carbonate is absent. It is evident that only on rare occasions will the conditions be such as to permit the filtration of the solution of the melt from an acid solution, and with compounds of unknown composition, it is impossible.

In the earliest attempts to determine the sulfur in rubber, Henriques oxidized with conc. nitric acid. Later, Alexander suggested sodium peroxide; Hinrichsen, a modification of Gasparini's electrolytic oxidation (afterwards improved by Spence); Waters and Tuttle employed conc. nitric acid and bromine; Pontio, manganese peroxide; Frank and Markwald, fuming nitric acid; and Kaye and Sharpe fused directly with zinc oxide and potassium nitrate. Some advocate a solution, others direct fusion, while practically all of those who had a preliminary wet oxidation added a fusion later. Solution without fusion is obviously a faulty procedure in the presence of lead and barium salts, and no data have as yet been presented to show that the direct fusion methods are accurate when the free sulfur is high. Of the methods employing both solution and fusion, that of Waters and Tuttle has given the most consistent results with all types of compounds, especially when some minor changes from that originally proposed are employed. The method recommended is as follows:

Place 0.500 gr. of rubber in a porcelain crucible of about 50 cc. capacity, add 20 cc. of conc. nitric acid saturated with bromine, cover the crucible with a watch glass, and allow it to stand for

one hour. Heat the crucible gently for one hour, then remove the watch glass, rinsing it with little water, and evaporate the solution to dryness (with pure gum compounds before evaporating add 0.1 to 0.2 gr. of potassium nitrate). Add 5 gr. of 1-1 mixture of sodium carbonate and potassium nitrate, and 1 or 2 cc. of distilled water; digest for a few minutes, and then spread the paste along the sides of the crucible, and dry on a steambath. Fuse the mixture, being careful to avoid contamination of sulfur from the flame. When the fusion is cold, place the crucible and contents in a beaker with about 250 cc. of water and heat for several hours; filter off the insoluble carbonates, washing with hot water. The total volume of the filtrate should be between 300 and 40 cc. Add 7 to 8 cc. conc. hydrochloric acid, cover the beaker, and heat on the steambath. Add 10 cc. 10% barium chloride, and allow to stand overnight; filter off the precipitated barium sulfate, ignite carefully over a Bunsen flame, cool and weigh. Calculate to sulfur, using the factor 0.1373.

The principal change from the published method is the addition of the potassium nitrate before evaporating off the nitric acid; it is necessary only in the absence of any basic fillers, and serves the purpose of changing any free sulfuric acid into potassium sulfate. With sulfuric acid, there is some danger of it being reduced by the organic matter, and sulfur lost as SO_2.

Probably the weakest feature of this method is the wear and tear on the crucibles, if this indeed can be considered a weak point. There are some makes of crucibles which will not last through a determination; on the other hand, some American and Japanese crucibles last through five to ten fusions. At this rate, the cost is negligible. It might be added further, in speaking of crucibles, that the smaller and thinner crucibles last longer than the thicker ones; much of the crucible trouble has been due to the use of extra large and thick crucibles, and to the use of inferior makes.

Occasionally, one finds the statement that the solution of the fusion should be evaporated to dryness with hydrochloric acid to get rid of the last traces of nitric acid, and to render insoluble the silica in the alkali silicates which have been formed. The small amounts of nitrates remaining after the fusion will not appreciably affect the accuracy of the determination and

dehydration of the silica is unnecessary, as Hillebrand[1] has shown. However, it is essential that the alkaline solution should be reasonably cool when the acid is added, that undue excess of acid be avoided, and that the solution be not allowed to concentrate to any large extent. We have frequently found considerable amounts of silica when the solution containing the precipitated barium sulfate had been allowed to concentrate to 50 cc. or less.

Allen and Johnston[2] have shown that the precipitate of barium sulfate formed in the presence of alkali chlorides and hydrochloric acid, is contaminated with chlorine and alkalies, and have worked out a method for correcting these errors, and so arrive at the true sulfur value. The precipitate obtained in the determination of total sulfur in rubber is subject to these same errors, but if the barium chloride be added rapidly to the hot solution, the solution never heated to boiling, and, further, if it is allowed to stand for at least 18 hours before filtering, the contamination will be low, and the fortunate balancing of errors will give results very close to the truth, so much so that it will not ordinarily pay to take the time for the corrections suggested by Allen and Johnston. It should be noted, however, that any attempt to improve the method of precipitation by eliminating only one of the errors, will yield results which are not as accurate as if the method was not changed.

If the free sulfur is low, the fusion method of the Joint Rubber Insulation Committee[3] will be found acceptable:

Mix 0.500 gr. of rubber with 4 gr. sodium peroxide and 6 gr. potassium carbonate in a dry 15 cc. iron crucible, and cover. Insert the crucible in a hole in a heavy brass plate so that about two thirds of the crucible projects through the hole. Heat cautiously until the first part of the reaction has taken place, and then increase the heat until the mixture fuses. Remove the flame and cool; place the crucible and cover in a porcelain casserole containing 200 cc. of water, add 5 to 10 cc. of bromine water, and boil until the melt is dissolved. Allow the precipitate

[1] Analysis of silicate and carbonate rocks, U. S. Geological Survey Bull. 422, p. 198.

[2] J. Am. Chem. Soc. *32*, 588-617 (1910); see also Richards and Parker, Proc. Am. Acad. *31*, 67 (1896); Hulett and Duschak, Z. Anorg. Chem. *40*, 196 (1904); John Johnston and L. H. Adams, J. Am. Chem. Soc. *33*, 829-45 (1911).

[3] J. Ind. Eng. Chem. *6*, 75-82 (1914).

to settle, decant the solution through a thick filter and wash with hot water.[4] Make the filtrate faintly acid with hydrochloride acid, heat to boiling, add 10 cc. of 10% barium chloride solution, allow to stand overnight; filter the barium sulfate as usual.

This method was originally recommended for testing insulated wire, in which the free sulfur was limited to 0.7%, and was found quite satisfactory. Tuttle and Isaacs[5] found that with high free sulfur, the results obtained were not accurate. It has been suggested that by increasing the quantities of sodium peroxide and potassium carbonate, even these high free sulfur samples could be analyzed without any trouble, but data are lacking in support of this contention.

It would be extremely desirable, from the time and labor-saving points of view, if the oxidation of the free sulfur and the fusion could be accomplished in one treatment. Spence's[6] electrolytic method eliminates the fusion, in the absence of lead and barium salts. Evans and Merling[7] have devised a method, using a Parr calorimeter: 0.200 gr. of rubber is packed in sodium peroxide, with some sugar and potassium chlorate. The ignited mass is extracted with water, filtered, acidified, and the sulfur precipitated as usual. The authors claim to have secured some excellent results so far, and the time required is very little, but it seems desirable that others test this method to discover its limitations, and faults, if it has any.

Free Sulfur.

The procedure to be adopted for determining the sulfur in the acetone extract depends largely upon the nature of the material, and whether it is desired to make further separation of the constituents in the extract. If not, the simplest, and yet the most accurate method we have, is as follows:

To the dried extract, add 100 cc. of water, and 3 to 5 cc. of bromine. (If a very high free sulfur is indicated by the character of the extract, the amount of bromine should be increased.) Allow the flask to stand for half an hour to an hour, boil off the bromine, and when the solution is practically colorless, filter

[4] The original method called for dehydration of silica, but, as previously noted, this is unnecessary.

[5] J. Ind. Eng. Chem. 7, 658 (1913).

[6] J. Ind. Eng. Chem. *4*, 413 (1912).

[7] India Rubber World, *64*, 658 (1921).

through a folded filter into a small beaker; cover the beaker, heat to boiling, add 10 cc. of 10% barium chloride, and after standing overnight, determine the barium sulfate as usual.

This method determines all of the sulfur in the extract; a great many checks have been run by taking the insoluble residue, fusing it with sodium carbonate and potassium nitrate, and determining the sulfur as is done in the Waters and Tuttle method, but the sulfur has never exceeded 0.01 to 0.02% in this residue. The oxidation is complete, rapid, requires no evaporation, furnishes its own acidity by the reaction with the barium chloride; in fact, after ten years, there still remains to be found some objection to its use.

If it is desired to make further examination of the acetone extract, the method of the Joint Rubber Insulation Committee[8] is recommended: the method starts where the acetone extraction has been treated with alcoholic potash, the alcohol removed, the residue taken up in water, extracted with ether, and the ether washed with water.

To the aqueous solution, add 2 gr. potassium nitrate; evaporate to dryness in a nickel or silver dish, and heat to quiet fusion. Transfer to a beaker, neutralize with hydrochloric acid, add 2 cc. of acid in excess, filter and wash, making the filtrate up to 200 cc. Heat to boiling, add a slight excess of barium chloride solution, allow to stand overnight, and determine the barium sulfate as usual.

Kelly[9] calls attention to the fact that what we have been determining as free sulfur is not the true free sulfur, but includes, in addition to the sulfur which may be said to be available for further vulcanization, such amounts of sulfur which may have been combined with the organic resins extracted by acetone. Obviously, this is so, and in the data presented by Kelly, which, however, covers only one compound, there is about 0.40% of sulfur combined with the organic matter in the extract. In such cases, the free sulfur as determined in the past is quite misleading. It is still a very great question as to whether the sulfur will always be of the same order of magnitude as Kelly indicates. It would have been very helpful if commercial samples had been

[8] Loc. cit.

[9] The determination of the true free sulfur, and the true sulfur of vulcanization; J. Ind. Eng. Chem. *12*, 875-8 (1920).

treated—in the many samples we have tested, we have frequently found samples where the free sulfur, as determined by the bromine method, was less than 0.10%. Upton[10] gives figures for free sulfur on some samples of insulated wire, determined by two methods, and several of these were below 0.20%, and in one case only 0.07%. Without questioning the force of Kelly's argument, it does seem as though we needed more data to show what variations there are between the free sulfur as at present determined, and the amount he calls the true free sulfur.

Kelly's method is as follows:

The acetone extraction is performed as usual. The acetone is driven off at not over 65C. To the residue, add 50 cc. of 75% alcohol which has been saturated with sulfur. Weigh the flask and contents to 0.5 gr. Heat for a few minutes, to get the organic matter in solution, and then cool slowly. Allow to stand three hours; reweigh, and add 75% alcohol, sulfur-free, to replace the loss. Decant the solution, wash two or three times with 75% alcohol saturated with sulfur, and then dry. The sulfur may then be determined by any satisfactory method.

No word is said as to what is to be done with the alcoholic solution of the resins; no scheme has been given for weighing them, and at 65C the extract would not be sufficiently dried to take that figure as the total acetone extract. If one knew just how much alcohol was used, and the sulfur it contained, the solution could be evaporated to dryness in a weighed flask, dried to constant weight at 90C, and the organic extract determined after making due allowance for the sulfur in the alcohol. As it stands now, the new method requires a separate extraction for the acetone extract.

Caspari[11] gives a similar method to the one used by Kelly. He uses petroleum spirit, boiling point 60-100C, which dissolves 3.0 gr. of sulfur per litre, whereas the 75% alcohol dissolves only 0.08 gr. Kelly says nothing about the accuracy when mineral rubber, tars, or paraffins are present, whereas Caspari speaks of the difficulty in getting these in solution. However, as we are interested only in separating the true free sulfur from the sulfur-carrying organic substances, it is quite within reason that undissolved paraffin would create no impassable difficulties.

[10] J. Ind. Eng. Chem. *10*, 518 (1918).
[11] India Rubber Laboratory practice, p. 116.

Sulfur of Vulcanization.

It is often desirable to know the amount of sulfur actually combined with the rubber during the process of vulcanization, both as regards determining the extent to which it has proceeded and to attain a greater uniformity in manufacturing practice. The simplest method for estimating uniformity, for comparative results, is by means of stress-strain curves, but mechanical defects operate to change values, so that comparisons are at best difficult and uncertain. The noticeable effect on the vulcanization by slight changes in sulfur content, demonstrate that the amount of sulfur which actually unites with the rubber is the controlling feature of the vulcanization. The value for the sulfur of vulcanization is necessary for the calculation of the total rubber hydrocarbons in some of the direct methods, and a further use is the possible discovery of the presence of reclaimed rubber in a rubber compound.[12]

Several possibilities are available; depending upon the nature of the rubber compound. The simplest case is that of pure rubber and sulfur, and occurs but seldom in commercial articles, although it is overworked as a formula for determining the value or properties of crude rubber. In this case, if the total sulfur is S, the free sulfur S_F, the percentage of rubber $100 - S$ then the sulfur coefficient, S_V will be:—

$$S_V = \frac{S - S_F}{100 - S}$$

In samples containing no organic sulfur compounds, the following method, based upon the determination of sublimed white lead by Schaeffer,[13] gives excellent results:

The sample is extracted with acetone for eight hours, and the free sulfur determined in the extract by the bromine method. The residue is placed in a porcelain boat, and transferred to a

[12] This is not as simple a proposition as it was before the rapid accelerators came into use. With inorganic accelerators, the proper cure for rubber was approximately at a coefficient of 3.0 to 3.5. and hence higher coefficients were fair indications of the presence of reclaimed rubber, especially in connection with other qualitative tests. Today, the value of the coefficient of vulcanization is almost nil, when, by the use of appropriate accelerators, good cures can be obtained with sulfur coefficients below 2.0. Of course, if one can learn what accelerator has been used, and determine the coefficient for the best cures with that accelerator, such data might be quite valuable in determining the condition of the rubber in the sample under observation.

[13] J. Ind. Eng. Chem. *4*, 837 (1912).

hard glass tube. Carbon dioxide is passed through the tube, which is then heated, gradually at first, and then at a dull red heat for a few minutes. The organic matter, together with the rubber, is distilled out, but the mineral sulfides and sulfates are unchanged. The sulfur in the fillers is determined by transferring the residue to a porcelain crucible, and determining the sulfur therein by the Waters and Tuttle method for total sulfur. The calculations for this method require a separate determination of rubber, R. Calling the sulfur in the residue S_R, then the sulfur coefficient will be calculated as follows:

$$S_V = \frac{S - (S_F + S_R)}{R}$$

This is the same formula as before, when $R = 100 - S$, and $S_R = O$.

The most difficult case is when, in addition to sulfides and sulfates, we have organic substances containing sulfur, such as oil substitutes, mineral rubber, etc. There are several procedures which may be followed, but the safest is probably to use Wesson's nitrosite method as revised by Tuttle and Yurow.[14] In his original article, Wesson says: "If the statement of Alexander[15] proves to be true that the sulfur of vulcanization of the rubber remains quantitatively in the nitrosite, this method could possibly admit of the simultaneous determination of the sulfur of vulcanization. An aliquot portion of the clear acetone solution of the nitrosite would be evaporated to dryness, and the sulfur determined in the usual way." A few attempts were made to determine the sulfur of vulcanization in this way, but not until after the errors which were contained in Wesson's method had been eliminated, was it possible to secure accurate determination of the rubber, and until then, little effort was made to determine the sulfur of vulcanization. When the final revision was in shape, determinations of the sulfur of vulcanization were found to check very well.

The sulfur coefficient figured by this method, is the result obtained by dividing the combined sulfur by the percentage of rubber hydrocarbons; such a calculation leaves no opening for

[14] As a matter of fact, this method can be used for any compound, and is not confined in its application to this single case where organic sulfur compounds are present: it is equally effective in rubber sulfur mixtures, and with mixtures containing mineral sulfur bearing fillers.

[15] *Z. Angew. Chem.* *20*, 1364 (1907) ; *24*, 687 (1911) ; Ber. *40*, 1077 (1907).

questions as to whether or not the sulfur was combined with the rubber, or with something other than rubber. It is simple, direct, and accurate.

When possible to make it, the direct determination of the sulfur coefficient (or for that matter any determination) is preferable to the difference methods, since all questions regarding interfering substances are eliminated. Kelly points out that not only is the figure usually determined as free sulfur really a mixture of elemental sulfur and sulfur combined with the resins and other soluble constitutents of the rubber, but that part of the sulfur insoluble in acetone is soluble in alcoholic potash. There seems to be no doubt that our use of the term free sulfur is not exactly correct; and that some of the residual sulfur should be removed by alcoholic potash seems equally reasonable, but, for ordinary length cures, the amount so removed is small (Kelly shows 0.07% for 2½ hours).

If we figure our coefficient on only the sulfur that is insoluble in alcoholic potash, obviously we should also take into our calculations the non-rubber constituents, and this would include the acetone soluble matter, or resins. In our formula, we would therefore have to correct R for the acetone extract A, and the alcoholic potash extract P, and we would have to deduct the sulfur in the alcoholic potash extract, S_P; hence, we would have the rather involved equation:

$$S_V = \frac{S - (S_F + S_R + S_P)}{R - (A + P)}$$

As a matter of fact, the relative amounts of rubber and non-rubber substances insoluble in acetone are such that even making this additional correction changes the coefficient very slightly, certainly within the limits of experimental error, as far as our experience goes. Hence, although no doubt the published data for coefficients of vulcanization are not absolute values, they are probably relatively accurate, and are comparable. Hence any deductions which may have been made from these data are no doubt just as valid as though every correction had been made.

Sulfur in Fillers.

The sulfur in fillers is determined as given under the method *for the determination of rubber by the ash method (cf. page 83).*

Chapter IX.

Detection of Organic Accelerators.

There is very little published work on this subject; probably a few laboratories have some special tests of their own, but as yet no one has seriously taken up this field. The data given below is largely from Twiss and Martin,[1] and Earle L. Reed.[2]

Paranitrosodimethylaniline. Extract about 10 gr. of the sample with acetone, and dry the extract; add 5 cc. dilute hydrochloric acid, shake thoroughly, and filter. A pink or carmine color results if p-nitrosodimethylaniline is present. If the filtrate is colorless, divide it into two portions, using one to test for aniline, and the other for hexamethylenetetramine.

The above test is a better negative than a positive test—if no color develops, the accelerator is not present, but there may be other organic bases which will give a pink color on acidification with dilute hydrochloric acid.

Twiss and Martin call attention to the color of the acetone extract which, however, is too common a color to use as an indication of an organic accelerator. A more positive test is to treat the dried acetone extract, or a dilute hydrochloric acid extract of a finely ground sample, with hydrogen sulfide water and ferric chloride solution, forming a blue, or greenish-blue, if paranitrosodimethylaniline is present. The reaction depends upon the reduction of part of the accelerator during vulcanization, to p-aminodimethylaniline, which, when treated as stated, forms methyleneblue.

Twiss gives the following alternative method: treat the hydrochloric acid solution of the dried acetone extract with a small piece of metallic zinc. Filter off the solution, cool thoroughly, and add a well cooled dilute aqueous solution of sodium nitrate. Add a small amount of this mixture to a solution of beta-napthol, with excess of aqueous sodium hydroxide. A deep blue results in the presence of p-nitrosodimethylaniline.

[1] Rubber Age, 9, 379-80 (1921).
[2] Unpublished data.

It can also be tested for by means of the Liebermann reaction. The dried acetone extract is boiled with a small amount of dilute caustic, and filtered; the filtrate is evaporated to dryness, conc. sulfuric acid and phenol added, the mixture diluted with water, and made alkaline with caustic potash, when a deep blue coloration will appear.

Aniline. Using the hydrochloric acid filtrate after testing for paranitrosodimethylaniline, add a drop of freshly prepared and filtered solution of bleaching powder. A violet color indicates the presence of aniline. Thiocarbanilide will ordinarily give no reaction to this test, unless present in very large amounts. It is well, in order to make sure of its absence, to take another portion of the dried extract, and heat, and look for the characteristic odor of thiocarbanilide.

Thiocarbanilide. A portion of the dried acetone extract is placed in a test tube, stoppered, and connected by a delivery tube with a second test tube containing two or three cc. of distilled water. The delivery tube must dip below the surface of the water. The first test tube is now heated until bubbles escape through the water in the second test tube, after which the heating is continued strongly for two or three minutes. Test the water in the second test tube for aniline with the filtered bleaching powder solution; a violet color will indicate thiocarbanilide if the original aniline test was negative.

Thiocarbanilide has a very characteristic odor, which is especially noticeable when heated. Heat the dried acetone extract, and compare the odor with that of some heated thio in a second test tube.

Hexamethylenetetramine. Using the second portion of the hydrochloric filtrate from the test for p-nitrosodimethylaniline, add 5 cc. of water, 1 cc. of phosphoric acid, a small amount of phenylhydrazine hydrochloride, 2 drops of 10% ferric chloride solution, and 2 drops of conc. hydrochloric acid. A cherry red color is produced by the formaldehyde from the hexamethylenetetramine.

Extract a ground sample with water, and test the extract for ammonia with Nessler's solution. A positive test indicates aldehyde ammonia or hexa—although some of the less commonly used accelerators may yield small amounts of ammonia, and hence respond to this test.

Diphenylamine. To the dried acetone extract from about 10 gr. of finely ground sample, add 2 cc. of conc. sulfuric acid, and agitate gently. Add a small crystal of sodium nitrate—a blue coloration results if diphenylamine is present.

This test can be made directly on light-colored compounds by placing a few drops of conc. sulfuric acid on the rubber to be tested, dipping a glass rod in dilute nitric acid, and touching it to the edge of the sulfuric acid.

Quinoidine. Treat the dried acetone extract with dilute sulfuric acid; quinoidine gives a blue fluorescence. Rochelle salts precipitate the tartrates of quinine or cinchonidine, but not quinidine. A saturated solution of potassium iodide added to an acid solution gives quinidine hydroiodide. Quinine and quinidine give the thalleioquin test, but cinchonine and cinchonidine do not; to a solution of the acetone extract in dilute sulfuric acid, add very weak bromine water, drop by drop, until a faint yellow persists, but avoid an excess of bromine; add ammonia, drop by drop, when a brilliant green color results. Making this solution acid turns the color to red.

General Tests. Extract 10 gr. of finely ground sample with dilute hydrochloric acid, cool thoroughly, and diazotize with cold dilute aqueous sodium nitrite. (The simplest scheme is to put a small piece of ice in the solution during the diazotizing; it can be removed later.) After a few minutes, pour a little of this mixture into a solution of beta-napthol in excess of caustic soda; a red precipitate or coloration indicates the presence of a primary aromatic amine, such as aniline toluidine, p-phenylenediamine, etc., or of derivatives of such bases with aldehydes (formaniline, methyleneaniline, benzylidene-aniline), and with carbon bisulfide (thiocarbanilide, or triphenylguanidine).

Chapter X.

Mineral Analysis.

The first step in a fillers determination of a rubber compound is to make a qualitative analysis of the metals which it contains. In this work, the color of the sample will be of considerable assistance in cutting out unnecessary steps, as will also a knowledge of the use to which the article is to be put. Only in the black compounds is there any necessity for making a fairly comprehensive examination.

Preparation of the Solution. The possible presence of lead, barium and calcium in a mixture containing sulfur (as sulfuric acid) makes the problem of making up a solution for qualitative analysis quite an interesting one. While several choices are open, the following procedure is recommended because of the fact that it permits quantitative separations to be made on a number of elements:

Place exactly 2.500 gr. of finely divided rubber in a porcelain casserole (about 250 cc. capacity), cover with 25 cc. of fuming nitric acid, and after standing in the cold for 15 to 30 minutes, covered with a watch glass, heat on a steam bath or hot plate until the rubber and all other organic matter is entirely destroyed. Potassium chlorate and fresh acid should be added from time to time. Evaporate the solution to dryness, add hydrochloric acid and a little water, and again evaporate to dryness and heat to dehydrate silica. Take up the residue with 50 cc. boiling water and 2 or 3 cc. of conc. hydrochloric acid. Filter into another porcelain casserole, and repeat the evaporation and dehydration of silica. Take up with 50 cc. of hot water, and 2 or 3 cc. of conc. hydrochloric acid as before, and filter. Unite the two portions of insoluble matter, and reserve for further treatment.

Heat the filtrate from the above, and add, drop by drop, 10 cc. of barium chloride solution until no further precipitate is formed, and then a few drops in excess. Allow to stand over-

night, filter off the barium sulfate (which may be discarded), wash well and transfer the filtrate to a 250 cc. graduated flask.

The insoluble portions reserved above are fused with sodium carbonate in a nickel crucible, cooled, and the melt taken up with distilled water. If lead, barium, or calcium sulfates were in the insoluble residue, they will now appear as insoluble carbonates, while the silica, if any, will be in solution. Filter off the insoluble matter, wash free from alkali, and then dissolve the carbonates off the filter with dilute hydrochloric acid and hot water. Filter through the same filter paper, and unite the filtrate with the solution already in the graduated flask.

The filtrate from the separation of the carbonates contains the silica; it should be evaporated to dryness, and the silica dehydrated and determined in the usual way. The filter paper from the filtration of the lead and barium should be ignited, and examined for silicates which may not have been attacked during the fusion.

The solutions united in the graduated flask are now made up to the 250 cc. mark at room temperature; 50 cc. of this solution contains the fillers from 0.500 gr. of rubber.

By this procedure, we have eliminated the sulfuric acid, which would prove so troublesome with lead, barium, and calcium, but in so doing, have introduced barium into the solution. This is of no importance, for barium is usually determined on a separate sample by a short but excellent method.

Another element is introduced through the fusion in a nickel crucible, but nickel is not likely to be found in rubber compounds so that we need merely eliminate it in its turn, and proceed with our analysis. On account of lead, fusion in platinum is impossible, while fusion in iron would introduce serious complications.

The object in making up a standard solution, is that 50 cc. may be taken for qualitative analysis, and further aliquot portions may be drawn for such quantitative tests as may be desired. In fact, with so few metals to be determined,[1] it is frequently possible to combine qualitative and quantitative separations at the same time.

If the silica is less than 0.5%, we may assume that it came

[1] Lead, iron, aluminium, zinc, calcium, and magnesium are practically the only metals to be determined. Antimony and barium are determined in special tests; manganese will be encountered where iron oxides are present, but is not necessarily determined.

from the talc used in dusting, and that the silica pigments, such as tripoli, talc, asbestine, aluminum flake, etc., have not been used as fillers.

The procedure for making the qualitative and quantitative separations may be taken from the standard text books, and need not be repeated here. A few words of caution may not come amiss.

In only two cases has vermilion been found amongst many hundreds of samples tested; it is too costly, and since it is used only for its color, there should be little difficulty in detecting this substance from the color of the compound.

Green-colored samples should be tested for arsenic, not that it is likely to be found, but merely to be on the safe side. Arsenic colors should never be used in rubber compounding, but it is well to see that no one is taking a chance.

Copper, even in traces, should be carefully looked for, because even in small amounts its deteriorating influence on rubber compounds is remarkable.

Note whether or not there is any appreciable quantity of magnesium; a small amount may be expected from the talc used in dusting stocks in the mill room, but it should be only a matter of 0.10% or so. More than that requires a quantitative determination, owing to the practice of using small amounts of magnesium oxide to activate organic accelerators.

If the nitric acid solution of the rubber shows insoluble material, and yet no silica is present, it indicates insoluble sulfates of lead or barium, or both.

Black specks remaining after the fuming nitric acid treatment of the rubber, indicates gas black or lamp black, for which a separate determination is made.

It will be seen from the description of the mineral fillers used in rubber manufacture, that the following metals may be found: antimony, lead, iron, aluminium, chromium, zinc, calcium, barium, magnesium, sodium, and ammonium salts. The compounds formed with these metals, consist of oxides, sulfides, sulfites, sulfates, carbonates, and silicates.

Oxides. The oxides are usually determined by difference; after the determination of the acid radicles, the excess of bases over that required to combine with the acids is assumed to be present as oxide.

Sulfides. Stevens[2] determines the sulfide sulfur as follows: The apparatus consists of a Kipp generator for carbon dioxide, a 250 cc. flask with an inlet tube reaching nearly to the bottom of the flask, and a ground-in stopper carrying an outlet tube (an all-glass wash bottle can readily be adapted for the purpose), and connected to the outlet tube are two absorption bottles containing lead acetate solution. Place in the flask 10 cc. of conc. hydrochloric acid and 20 to 30 cc. of ether, pass a current of carbon dioxide through the apparatus until all air is removed, then remove the stopper and add the sample (0.1 to 1.0 gr., depending upon the amount of sulfide expected; where nothing is known regarding the sample, use 1.0 gr.). Again pass carbon dioxide through the apparatus for about 30 minutes, with an occasional shaking of the flask. During this period, the hydrochloric acid attacks the sulfides, liberating hydrogen sulfide, which is carried over to, and absorbed by the lead acetate solution. The purpose of the ether is to swell the rubber, and facilitate the penetration of the acid to all parts of the sample.

Heat gently to drive off the ether and the final traces of hydrogen sulfide. Reserve the solution in the flask for the determination of sulfate sulfur. All of the sulfide sulfur is now combined with the lead.

Stevens determines the sulfur from this point by adding acetic acid to the lead acetate solution in order to decompose the carbonates formed, the lead sulfide is filtered off, and washed free from lead salts, transferred to a stoppered flask, a standard iodine solution added, and after the reaction is complete the excess of iodine is titrated with sodium thiosulfate. However, any other accurate method will answer the purpose; the lead sulfide may be dissolved in nitric acid, taken to fuming with sulfuric acid, and the lead sulfate determined gravimetrically.

If pure nitrogen is available for sweeping out the apparatus, it will be found to be much simpler to use sodium hydroxide for absorbing the hydrogen sulfide; the solution can be oxidized with bromine, and after acidification, the sulfate can be precipitated with barium chloride; altogether, much simpler, and probably more accurate than the lead acetate method.

Sulfide sulfur, excepting antimony sulfides, may also be determined by the ignition method of Schaeffer, transferring the resi-

[2] Analyst, *40*, 275-81 (1915).

due to a flask similar to the one recommended by Stevens, and proceeding as directed by him for driving over the hydrogen sulfide. This procedure is best for lead sulfide; antimony and mercury sulfides sublime unchanged.

Sulfites. Sulfites and sulfates are transposed by heating with sodium carbonate. Schaeffer gives the following method for determining the sulfite-sulfur in sublimed blue lead:

Boil 1.5 gr. of the sample with 3 gr. of sodium carbonate; allow to stand, filter, and wash thoroughly. To the filtrate, add 3 cc. of bromine water, heat gently to oxidize the sodium sulfite to sulfate, and precipitate the sulfate with barium chloride. The barium sulfate formed will contain both the sulfur present as sulfite, and sulfate; deduct the amount of sulfur present as sulfate from the total, and the remainder is calculated to lead sulfite. (See determination of sulfates in the presence of sulfites, under sulfate-sulfur.)

Sulfates. Stevens determines the sulfate-sulfur in the residue from the determination of sulfides, as follows: Extract the residue with hydrochloric acid until no further material can be dissolved; unite the filtrates, and determine the sulfur as usual. It will be noted that by this means Stevens dissolves out only the lead sulfate and calcium sulfate; barium sulfate will be only slightly attacked. This method is therefore not applicable for the determination of lithopone, for example, or in any other case where barium sulfate is present along with some sulfide.

We again find Schaeffer's ignition process of value in determining the sulfates. Boil the ignited residue with sodium carbonate as directed under sulfite-sulfur, and filter. The function of the bromine water in the sulfite determination is to oxidize the SO_2 to SO_3; if instead of adding bromine water we add hydrochloric acid, and boil the solution, the sulfur dioxide will be driven off, and we will have remaining only the sulfate-sulfur.

Carbonates. Carbonates can be determined in an apparatus similar to Stevens' arrangement for sulfide-sulfur. Instead of a Kipp generator, we use air which has first been passed through a soda-lime tower, to remove traces of carbon dioxide. In this case, the absorption train consists of two absorption bottles containing conc. sulfuric acid and potassium bichromate (a and b); two soda-lime tubes (c and d); and the fifth tube containing sulfuric acid and bichromate (e). It is vital in this determination

that tubes b and e should be frequently refilled, and from the same solution; only with such precautions are we able to maintain the air at the same moisture content when it leaves e as when it entered c. Tubes c, d, and e, are weighed before and after the determination; the increase in weight is the carbon dioxide. Cases are known where d actually lost weight, owing to the fact that c absorbed all of the CO_2, and the air withdrew from d some of its moisture, which, however, was reabsorbed by e.

Any similar arrangement will do just as well, providing[3] the gas used to wash the apparatus contains no carbon dioxide, or organic matter which might be oxidized by the sulfuric acid-bichromate mixture; the absorption tubes are adequate for the purpose; and the balance of the moisture content of the gas is preserved.

Silicates. These have already been separated by the method of getting the metals of the fillers into solution. It is only necessary here to repeat that all of the silica is not obtained by the first dehydration and treatment with hydrochloric acid, no matter how long the process be continued; the operation must be repeated or the error will show up in the determination of the other constituents.

Special Determinations.

The qualitative and quantitative analyses made as prescribed in the preceding paragraphs will suffice for the determination of most of the metallic bases, or fillers, but some of these are better determined by special tests; amongst the mineral fillers we find in this list the antimony compounds, lead chromate, barium carbonate, etc., and amongst the organic, carbon black, blue, etc.

Antimony. The principal trouble with antimony is getting it into solution without loss. There should be little difficulty once this has been accomplished. Rothe[4] treats the sample with 10-20 cc. conc. nitric acid and 2 cc. sulfuric, and heats for 1 to 2 hours at a moderate heat; then increase the heat until all nitric acid is driven off and the sulfuric acid fumes strongly. More nitric acid is added, and taken to fuming, and this operation is repeated until the absence of darkening shows that the

[3] For a more complete discussion on this point, see Tuttle and Yurow. "The Direct Determination of Rubber by the Nitrosite Method," U. S. Bureau of Standards Tech. Paper, No. 145 (1919).

[4] Chem. Ztg. 33, 679 (1909).

organic matter is destroyed. Dilute to 100 cc. and boil to expel all nitric fumes. Schmitz[5] takes from 2 to 4 gr. of finely cut rubber (Frank and Marckwald think the quantity is too high, as it no doubt is for most antimony compounds), and treats it in a Kjeldahl flask with 15 cc. conc. sulfuric acid per gram of rubber. One drop of mercury and a small piece of paraffin (to prevent foaming) are introduced. Heat until the solution starts to clear; add 2-4 gr. of potassium sulfate, and heat until colorless. Cool, dilute with water, add 1 to 2 gr. of potassium bisulfite, with excess of tartaric acid; heat until no sulfur dioxide remains, add dilute hydrochloric acid, filter, and titrate the antimony. Wagner[6] fuses in a porcelain crucible, 0.5 to 1.0 gr. of rubber with 5 gr. of 1-4 sodium nitrate-potassium carbonate. The rubber is mixed with part of the fusion mixture, placed in the crucible, and covered with the remainder. The heat must be applied gradually, and if any organic matter remains, more sodium nitrate must be added, and the whole reheated. Wagner claims good results, but the method looks risky; the danger of loss of antimony by excessive heating is very great. When zinc oxide or sulfide are present, Frank and Marckwald[7] separate the rubber from the fillers with xylol; otherwise, they oxidize the organic matter with conc. nitric acid and potassium chlorate, finally evaporating with hydrochloric acid. If organic matter is still present, it must be eliminated. The antimony is precipitated as sulfide, and weighed as such. Collier, Levin and Scherrer[8] take advantage of the simultaneous determination of the fillers by the cymene method to determine the antimony after the rubber has been dissolved out. Their method is as follows:

Extract 0.500 gr. of the sample with acetone for 8 hours, and with chloroform for 4 hours. Dry the residue in a vacuum desiccator, transfer to a 300 cc. lipped assay flask, add 25 cc. of cymene, and heat on an electric hot plate at 130-140C until the rubber is dissolved. Cool the flask, dilute with 250 cc. of petroleum ether, and allow to stand overnight. Filter by decantation through a tight Gooch pad of asbestos, previously washed with alkali, conc. hydrochloric acid, and water, and dried. Wash by decantation with petroleum ether until the filtrate is colorless.

[5] Gummi Ztg. 25, 1928-30 (1911).
[6] Chem. Ztg. 30, 638 (1906); J. Soc. Chem. Ind. 25, 583 (1906).
[7] Gummi Ztg. 23, 1046 (1909).
[8] Rubber Age, 8, 104-5 (1920).

Add 30 cc. of conc. hydrochloric acid to the assay flask, and shake until all of the antimony sulfide has gone into solution; filter slowly through the Gooch, using gentle suction. Wash thoroughly, and dilute the filtrate to 250 cc. with hot distilled water, pass in hydrogen sulfide until the antimony has been completely precipitated.

After the solution of the antimony has been effected, it may be determined by any of the well known methods. Wagner, and Frank and Marckwald weigh as sulfide, Schmitz recommends titration, as do Collier, Levin and Scherrer. The methods recommended by the last named are as follows:

Filter off the antimony sulfide, wash with hydrogen sulfide water, and transfer the precipitate to the filter paper. Place 20 cc. of concentrated hydrochloric acid in the beaker, and set aside temporarily. Transfer the antimony sulfide and the filter paper to a Kjeldahl flask, add 12-15 cc. of concentrated sulfuric acid and 5 gr. of potassium sulfate, place a funnel in the neck of the flask, and heat until the solution is colorless. Wash the funnel, and dilute the solution to about 100 cc. with water, add 1-2 gr. of sodium sulfite, transfer the hydrochloric acid in the beaker in which the antimony sulfide was precipitated to the Kjeldahl flask, and boil until the sulfur dioxide is all driven out. Dilute to 250-275 cc. with water, cool to 10-15C, and titrate with permanganate until a faint pink color is obtained.

Instead of filtering the antimony on filter paper, it may be filtered on a Witt plate and asbestos. Transfer the plate, pad and precipitate to an Erlenmeyer flask; remove any antimony sulfide adhering to the beaker or funnel with hydrochloric acid. Wash the beaker and funnel with hot distilled water, dilute the solution to 250-275 cc., add 12 cc. of concentrated sulfuric acid, boil the solution until no trace of hydrogen sulfide is obtained with lead acetate paper, cool to 10-15C, and titrate with standard permanganate solution.

Barium Salts. Ignite a 1 gr. sample in a porcelain crucible, cool, add 3 to 5 drops of nitric acid and 1 cc. of water, and stir into a paste, add 5 gr. of 1-1 potassium nitrate-sodium carbonate, dry on the hot plate or steam bath, fuse until the melt is soft or pasty; allow it to cool, extract with hot water, and wash with hot water containing a little sodium carbonate. Dissolve the insoluble carbonates in hydrochloric acid, and wash the filter paper

thoroughly. Nearly neutralize the filtrate with sodium carbonate, and pass hydrogen sulfide through the solution until the lead is entirely precipitated. Filter, heat the filtrate to boiling, and add 10 cc. of 10% sulfuric acid; allow the precipitate to stand overnight, and determine the barium sulfate as usual.

The only troublesome element is lead, and it may be completely eliminated. Check determinations of 0.10% of the barium sulfate present may easily be obtained.

In some specifications, a maximum limit is placed on the total sulfur, but barytes is a permissible filler, without having the sulfur which it contains count as part of the total sulfur. In such cases, the determination of barytes is obligatory; if made by this method, the error in the total sulfur caused by the correction will not exceed 0.02%.

Barium Carbonate.[9] Place 1 gr. of the sample in a porcelain boat, and ignite in an atmosphere of carbon dioxide as described by Schaeffer.[10] After ignition, and when the ash is at room temperature, remove the boat, grind the ash to a fine powder in an agate mortar, transfer to a 250 cc. beaker, cover with 5-10 gr. of ammonium carbonate, 15-20 cc. of strong ammonia, and 50 cc. of distilled water. Ammonium carbonate transposes lead sulfate into lead carbonate, but is practically without action on barium sulfate. Boil the mixture for 15 to 30 minutes, filter, and wash the precipitate thoroughly to remove all soluble sulfates. Wash the residue on the filter paper back into the original beaker with distilled water, add 10 cc. glacial acetic acid, and sufficient water to make the volume up to 100 cc. Heat to boiling, and filter through the same filter paper as before. Lead, barium calcium and zinc carbonates pass into solution, whereas lead sulfide and barium sulfate are not attacked. Pass hydrogen sulfide into the filtrate, filter off the lead sulfide, heat the filtrate to boiling, and

[9] The reason for working out a method for determining barium carbonate is not without interest. In material made under specifications, some manufacturers evidently desired to use compounds which contained more than the prescribed amount of sulfur. Realizing that the specifications exempted the sulfur in the barytes from counting in the total sulfur, and knowing that the barium sulfate was being estimated from the amount of barium found by analysis, they felt that by adding barium carbonate, they would receive credit for sulfur equal to the barium in the carbonate, and thus bring the total within the specification limit. The trick was first discovered when after correction for the sulfur supposed to be present in combination with the barium, the total sulfur was actually less than the free sulfur.

[10] Cf. page 91.

precipitate the barium with 10 cc. of 10% sulfuric acid. Allow to stand overnight, and determine the barium sulfate as usual.

If barium sulfate and no carbonate is present, a small amount of precipitate will be found, showing a slight solubility of the barium sulfate, or else reduction of the sulfate to sulfide. The amount will usually be less than 1% of the amount of barium sulfate present. In a mixture of the two, the carbonate will run somewhat high, for the same reasons, but with proper attention to details the results will be quite sufficient for every purpose.

Gas Black or Lamp Black. Chemical analysis alone will tell nothing as to whether gas black or lamp black has been used. Even the microscope is, as yet, of little value in distinguishing between the two, and the only thing remaining for us to do is to determine the total carbon, and assume from the physical properties of the article, whether or not the black is gas black or lamp black.

The free carbon is determined as follows: [11]

Extract 0.5 gr. of rubber for 8 hours with a mixture by volume of 68% chloroform and 32% acetone. Transfer the sample to a 250 cc. beaker, and heat until it no longer smells of chloroform. Add a few cc. of hot conc. nitric acid, and allow to stand in the cold for about 10 minutes. Add 50 cc. more of hot conc. nitric acid, taking care to wash down the sides of the beaker; heat on the steam bath for at least an hour. While hot, decant the liquid through a Gooch containing a thick pad of asbestos, taking care to keep the insoluble material completely in the beaker. Wash with hot nitric acid, and suck dry. Empty the filter flask. Wash the insoluble residue with acetone, and then with a mixture of equal parts of acetone and chloroform, until the filtrate is colorless. The insoluble matter, which has been carefully retained in the beaker, is digested on the steam bath for 30 minutes with 35 cc. of a 25% solution of sodium hydroxide. Dilute to 60 cc. with hot water, filter the solution, and wash with a hot 15% solution of sodium hydroxide. Test for the presence of lead by running some warm ammonium acetate solution containing an excess of the hydroxide through the pad into sodium chromate; if a yellow precipitate is obtained, the pad must be washed until the washings no longer give a precipitate with the sodium chromate

[11] Smith and Epstein, U. S. Bureau of Standards Tech. Paper, No. 136; J. Ind. Eng. Chem. *11*, 33-6 (1919).

solution. Next wash the residue a few times with hot conc. hydrochloric acid, and finally with warm 5% hydrochloric acid. Remove the crucible from the funnel, taking care that the outside is perfectly clean, and dry in an air bath at 150C to constant weight. Burn off the carbon at a dull red heat, cool and reweigh; the difference in weight is approximately 105% of the carbon originally present in the form of lampblack or gas black.

Several points must be carefully watched during this procedure: the acetone and hot nitric acid must not be brought together, since they react with considerable violence. Again, care must be used in the alkali washing to avoid carrying through the filter some of the gas black; the pad must be unusually thick and free from channels. This is one of the principal reasons for keeping the fillers in the beaker until the last moment.

The published data of Smith and Epstein show that the loss in weight on ignition is about 5% higher than the carbon actually present; hence the factor 105. The 5% is probably organic matter not removed by the preliminary steps of the method. Mineral rubber has no effect on the determination. Calcium sulfate, if retained with the fillers, would be reduced during the ignition of the carbon, and would give high results for the latter. Quite apart from the point raised by Smith and Epstein that calcium sulfate is rarely found in rubber compounds, usually only when associated with antimony, the treatment with strong acids, and boiling, would suffice to dissolve out a considerable quantity of calcium sulfate, which is quite soluble in hot nitric or hydrochloric acid solutions.

Red Lead. The peroxide of lead contained in red lead is not a particularly desirable constituent for rubber compounds, and some specifications, notably those for 30 or 40% Para insulation, forbid its use. The Joint Rubber Insulation Committee[12] gives the following test for red lead: Dissolve a 1 gr. sample, previously extracted with acetone, in xylol; when the rubber has been completely dissolved, filter through a Gooch crucible, washing thoroughly with benzol, alcohol and acetone. Transfer the Gooch pad to a distilling flask, add hydrochloric acid, and distil over the chlorine into a potassium iodide-starch solution. If more than 0.1 cc. of N/10 sodium thiosulfate is required to titrate the iodine liberated, red lead may be assumed to be present.

[12] J. Ind. Eng. Chem. 6, 75-82 1914).

This method was suggested for insulation compounds, and, as far as it has been tested, has given satisfactory results. The method depends upon the liberation of chlorine by the action of the peroxide on the hydrochloric acid. Some off-color litharge samples have given positive tests under this method; which is what we might expect, since these lots contain a greater amount of peroxide than they should, and yet not enough to be classed as red lead. They are really mixtures of red lead and litharge, and should be so treated.

Chromates, such as chrome yellow, will give this reaction, but they should cause no confusion, since the color of the sample will usually tell whether chromates are present. It would be unusual indeed to have both chromates and lead peroxide present in the same sample.

Chromates. While chromium is not a frequent constituent of rubber goods, it is a possibility, and should be determined. There is considerable analogy between the analyses of the pigments in printing inks, and those in rubber compounds, and the following method, originally used in the analysis of printing inks, should be equally available for rubber compounds.

Fuse 0.500 gr. of rubber with equal parts of sodium peroxide and potassium carbonate, using a nickel crucible. The heating must proceed cautiously until the organic matter is destroyed, after which the melt can be heated strongly for 10 or 15 minutes. Cool, extract with water, and filter. The chromium is in the filtrate as chromate. Pass carbon dioxide through the filtrate, and heat on the steam bath, in order to precipitate any lead which may be held up by the caustic alkali; filter if necessary. Cool, acidify strongly with hydrochloric acid, add potassium iodide and starch solution, and titrate with standard N/10 sodium thiosulfate to a colorless solution. The solution may be standardized against potassium bichromate, and the chromium calculated to CrO_3, in which condition it no doubt exists in the compound.

This method has been found simple and accurate in the presence of lead, manganese, clay, and other fillers likely to be present in printing inks, and should be fully as satisfactory for rubber goods.

Glue. Make a qualitative test as follows: Digest 1 gr. in cresol, or xylol (any solvent for rubber which does not attack

glue will do just as well) until the rubber is decomposed. Dilute with petroleum ether, and filter through filter paper. Wash the residue with alcohol, and after allowing the alcohol to evaporate wash the residue back into a beaker, cover with water, and boil. Filter off the insoluble, and test the filtrate for glue with a solution of tannic acid. Traces of glue will give only a milky cloudiness, but with large quantities a heavy precipitate is thrown down.[13]

The quantitative determination of glue is based on the determination of nitrogen by the Kjeldahl method. This procedure assumes that the principal source of nitrogen, the organic accelerators, will be removed during the acetone extract. The U. S. Bureau of Standards extracts with the mixed solvents, 68% by volume of chloroform, and 32% of acetone. From this point on, the procedures are alike: the dried sample is heated with sulfuric acid, potassium or sodium sulfate and a small amount of copper sulfate, the clear solution is diluted, made alkaline, and the ammonia distilled into a standard solution of N/10 sulfuric acid.

Practically every one is agreed that the Kjeldahl method is the most satisfactory means of approach in the quantitative determination of glue, but differences arise as to the factor by which to calculate from nitrogen to glue. The Bureau of Standards uses 5.56; others prefer the factor of 6.25. Since glue is not a pure chemical substance, we are bound to have differences of opinion, but the weight of evidence seems to lean towards the higher factor. The collagens have 17.9% of nitrogen, and even assuming that in glue we have reasonably pure collagens, we must take into consideration the water which is always present, and which will average about 10%, hence, in the collagens, 5.56 would be the correct figure, and calculating that this is only 90% of the whole, we get 6.18 as the corrected figure.

Another variable will be the amount of nitrogen in the insoluble matter in the rubber, which, as we have already discussed, may run from 2 to 6% of the rubber, and may contain from 10 to 18% of nitrogen.

In view of the above facts, it is obvious that any factor will

[13] A much shorter method of testing qualitatively for glue is as follows: Heat 5 to 10 gr. finely divided sample of rubber with 25 cc. of water for 2 to 4 hours; decant, and test for glue with 2 or 3 cc. of a solution of tannic acid. This test is not as safe as the one given above; glue to the extent of 2 or 3% may be easily overlooked, and hence the method is not recommended.

at best give only an approximation of the truth, but, even so, it is believed that better results on the average will come from the use of the factor 6.25, and which we recommend.

Ground Organic Wastes. In a mixture of rubber and wastes, containing such materials as leather, cork, wool, silk, cotton or other vegetable fibre, etc., the separate determination of these wastes is usually of no consequence, and a direct determination of the rubber by the nitrosite method will give practically all the information that one really needs. Some of the solvents, such as xylol, cymene, and possibly others, will determine the rubber accurately enough in the presence of such materials.

There are occasions when we may be called upon to determine cotton, as for example, in balloon fabrics, where it is difficult to separate the rubber from the cotton, etc. For this purpose, the method of Epstein and Moore [14] will suffice:

Treat a 0.500 gr. sample of the rubber with 25 cc. of freshly distilled cresol (b.p.198C) for 4 hours at 165C. Cool, add 200 cc. of petroleum ether very slowly, and with constant agitation. Filter through a Gooch, and wash with petroleum ether, then with hot benzene, and finally with acetone. Add hot 10% hydrochloric acid, and transfer the contents of the flask to the Gooch, and wash at least ten times with hot acid. Wash free of chlorides, and then with acetone until the filtrate is colorless. Wash with a mixture of equal parts of acetone and carbon bisulfide. Wash with alcohol, and dry for 1½ hours at 105C. Transfer the asbestos pad and fillers to a weighing bottle, dry for about 10 minutes further, cool and weigh.

Transfer the contents of the weighing bottle to a 50 cc. beaker and pour over it 15 cc. of acetic anhydride and 1 to 2 cc. of conc. sulfuric acid, and digest on the steam bath for one hour. Cool, dilute with 25 cc. 90% acetic acid, and filter through a weighed Gooch. Wash with hot 90% acetic acid until the filtrate is colorless, and then four times more. Wash about 5 times with acetone, remove the crucible from the funnel, and dry to constant weight at 150C. The cellulose has been dissolved out, and the usual calculations are made.

Sponge Rubber. One of the interesting points in connection with the analysis of sponge rubber is to determine the substance

[14] U. S. Bureau of Standards Tech. Paper, 154; The Rubber Age, 6, 289-93 (1920).

used to produce porosity. Organic liquids, if used, will have been dissipated by the time the sample reaches the analyst. If either ammonium carbonate or sodium carbonate has been used sufficient material will usually remain to give a qualitative test, although a quantitative determination is out of the question.

Grind the sample into small particles, being particularly careful to avoid heating. Digest 10 gr. of the sample in 25 cc. of water for one hour, and filter. Divide into two portions; into the first, add 10 cc. of 20% caustic soda, and note any odor of ammonia which may escape. A positive test indicates ammonium carbonate. A more delicate test may be made by adding a little hydrochloric acid, and evaporating to dryness, and treating the dried residue with a small amount of strong alkali. Evaporate the second portion of the extract to dryness, take up with 25 cc. of water, and add a few drops of methyl orange. Titrate with N/10 hydrochloric acid; any appreciable quantity of alkaline carbonate, in the absence of ammonia, will be a fair indication that sodium bicarbonate was used. In case ammonium carbonate was used, the residue from the second filtrate should be heated strongly to remove the ammonia, and thus determine whether both substances were used.

Negative tests for both ammonium carbonate and sodium bicarbonate may be taken to indicate that organic liquids have been employed.

Specific Gravity.

Rubber Compounds. For ordinary rough work, where great accuracy is not necessary, and when pieces of from 2 to 5 gr. are available, Young's gravitometer is a rapid and convenient instrument. When the bearings are clean, and the instrument in good working order, the results are usually with 0.02, plus or minus and are frequently only half that.

For greater accuracy, the pycnometer is the best thing to use. Weigh out about 5 gr. in small strips, place them in the pycnometer bottle, and fill with distilled water to the mark, being careful that no bubbles adhere to the rubber, and then weigh. Knowing the weight of the bottle filled with water, the weight of water displaced by the rubber is easily calculated, and from this, the specific gravity of the rubber. Ordinarily the specific gravity is expressed to two decimal places, but even without

bringing the pycnometer to constant temperature, the calculations may be made to the third decimal.

It has been found convenient, both in using Young's gravitometer and the pycnometer, to wet the rubber with a soap solution, brushing it on with a camel's hair brush, and then rinsing the rubber with distilled water. It eliminates the risk of air bubbles, and does not affect the accuracy of the determination.

Pigments and Fillers. Pigments in lumps may be handled as in the case of rubber compounds; the pycnometer is probably better for the purpose.

Oils are determined with the Westphal balance, or, for quicker and less accurate work, a hydrometer will do.

For powders, or small particles, the pycnometer is required. The liquid chosen must be such as to have no effect on the pigment being tested. For many of them, water will answer, but where this is impossible, any other liquid will do just as well, providing it does not react with, or dissolve the pigment. With liquids other than water, the coefficient of expansion may be such as to make it imperative to hold to a standard temperature of say 25C, the specific gravity being referred to water at that temperature.

Weigh out 5 gr. of the pigment, transfer to a pycnometer, and fill the latter about two-thirds full. Boil the liquid for 10 to 15 minutes, and then place under a vacuum bell jar. When the air has been entirely removed from the sample, cool to room temperature (or to a standard temperature of 25C), fill up to the mark, and weigh. When a liquid other than water is used, determine its specific gravity as referred to water at 25C, and use this to calculate the gravity of the pigment.

Reclaimed Rubber. One of the important values connected with reclaimed rubber is its gravity, and yet it is frequently so porous that ordinary methods fail to secure accurate results. In thin sheets, and with boiling water, fair results may be obtained. When a small mixing mill has been available, the following scheme has been found eminently satisfactory:

Mix 450 grams of reclaimed rubber and 50 grams of sulfur, until thoroughly and evenly mixed. The total weight of the batch after mixing should be within 1 gr. of 500. Vulcanize a small strip from the mix, and from this strip determine the specific gravity of the mixture. Calculate the specific gravity of

the reclaimed rubber, taking the specific gravity of sulfur as 2.0. If the specific gravity of the mixture is a, and the specific gravity of the reclaim x, the calculation is as follows:

$$x = \frac{100a - 20.00}{90}$$

For example, if the gravity of a mixture is 1.370, the calculation would be:

$$x = \frac{100 \times 1.370 - 20.00}{90.} = \frac{117.00}{90.00}$$

$$x = 1.30$$

A chart can be drawn, so that given the specific gravity of a mixture that of the reclaimed can be read off directly. A different mixture of reclaimed rubber and sulfur may be employed, making the necessary alterations in the formula, the only requisite being that there should be sufficient sulfur for vulcanization.

Chapter XI.

Microsectioning and Microphotography.

Microphotographs of rubber goods have been known for a number of years, Weber showing some excellent photographs of hard and soft rubber goods in his book on India Rubber. Recently, there has been considerable attention paid to the use of the microscope in mineral analysis of small amounts of materials, and in the examination of commercial materials, mixtures, etc. It has been realized that the chemical analysis does not give the last word, and that frequently the difference in the properties of two materials may be a matter of their physical state, rather than their average chemical composition. In the rubber industry, many laboratories have been working along the lines of preparing sections of rubber compounds thin enough to be examined under transmitted light, instead of reflected light, as

results. Sections thinner than 1μ are now being prepared, a great deal of work has been started, and we are beginning to see the fruits of this work.

Liquid air is probably not available for many laboratories, but in such cases the use of carbon dioxide alone will be found to give results well worth the effort, even though better could be obtained with the cooling effected by the liquid air.

Perhaps one of the most interesting points brought out by this new phase of rubber testing came to light at the meeting of the American Chemical Society at Rochester, in April, 1921. Schippel[1] had previously shown by experiment that compounded and vulcanized rubbers showed an increase in volume on stretching, and his explanation was that vacu were formed around the mineral particles, caused by the rubber being pulled away from the surface of the pigment. Green[2] exhibited some microphotographs of sections of rubber under strain, wherein the vacu were caused by the rubber leaving the surface of the pigment [illegible] the evident fact that [illegible]menon.

Chapter XI.

Microsectioning and Microphotography.

Microphotographs of rubber goods have been known for a number of years, Weber showing some excellent photographs of hard and soft rubber goods in his book on India Rubber. Recently, there has been considerable attention paid to the use of the microscope in mineral analysis of small amounts of materials, and in the examination of commercial materials, mixtures, etc. It has been realized that the chemical analysis does not give the last word, and that frequently the difference in the properties of two materials may be a matter of their physical state, rather than their average chemical composition. In the rubber industry, many laboratories have been working along the lines of preparing sections of rubber compounds thin enough to be examined under transmitted light, instead of reflected light, as had been so largely the practice. The problem very quickly narrowed itself down to a question of mechanical manipulation, for even the crude sections first prepared showed that the procedure was feasible, and that information could be obtained not only regarding composition, but even the properties of rubber compounds, if the proper sections could be prepared.

The microsectioning has largely been done with the Spencer microtome, which seems adequate for the purpose. The main difficulty has been to so stiffen the rubber compound that it would have no motion when being cut. Freezing was resorted to, the earliest attempts employing the expansion of carbon dioxide directly on the stage of the microtome, or surrounding the specimen to be cut with solid carbon dioxide. Further stiffening of the rubber was obtained by imbedding it in such materials as starch paste, water-glycerine solutions, paraffin, etc. The best results are obtained with material which does not become brittle at the low temperatures employed. Even carbon dioxide cooling was found to be insufficient for the purpose, and the use of liquid air was resorted to, with eminently satisfactory

results. Sections thinner than 1μ are now being prepared, a great deal of work has been started, and we are beginning to see the fruits of this work.

Liquid air is probably not available for many laboratories, but in such cases the use of carbon dioxide alone will be found to give results well worth the effort, even though better could be obtained with the cooling effected by the liquid air.

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The work of Breyer and his coworkers Ruby, Depew, and Green, and of I. C. Diner, should shortly put us in a position where we can take a piece of rubber and at least qualitatively tell what pigments are present. It is too much to expect anything in the quantitative line, especially when one considers the extremely small area covered by these microphotographs, and the difficulty of securing even mixing of a plastic such as rubber with dry fillers. We know that we have variations in composition from one part of a batch to another; and this variation must be very much greater when the sample under observation weighs less than a milligram. It is quite within the range of probability that we shall, by careful sectioning, be able to tell whether we are dealing with carbon black or lamp black; and particularly identify such substances as Tripoli, aluminum flake, talc, asbestine, etc., in mixtures of two or more, under which

[1] J. Ind. Eng. Chem. *12*, 33-7 (1920).

[2] Henry Green. "Volume increase of compounded rubber under strain," Rubber Division, American Chemical Society, Rochester, April, 1921.

conditions the identification by chemical or mechanical means is practically impossible.

The general scheme for the examination of microsections[3] deals with (*a*) reflected light; (*b*) transmitted light; (*c*) polarized light. With reflected light, we use not only vertical, but oblique rays, so as to get some idea of the surface, as well as the color of the section. In transmitted light we have a new color classification, wherein some fillers which are opaque and colored in reflected light may be translucent and show a different color by transmitted light. In polarized light, we have the differences in optical behavior between crystalline and non-crystalline substances; interference figures, extinction angles, etc., to further classify the materials under observation. Considering the comparatively limited number of substances one finds in rubber compounds, as compared with the entire mineral field, the possibility of exact identification is very great.

As far as the identification of fillers is concerned, the future seems bright, and today practically all the work is being conducted along these lines. We have still to consider the possibility of identifying different rubbers, or the rubber plastics, such as the mineral rubbers, substitutes, etc., reclaimed rubber, softening oils and waxes, etc. For some of these substances, notably mineral rubber, paraffin, rosin, oil substitutes, we have excellent chemical means of identification, and more or less accurate means for their quantitative determination. The problem of the identification of reclaimed rubber, and the different grades of new rubber, is still open for solution, and it may be that this new means of research will prove of valuable assistance in investigations of this sort.

[3] Some excellent text books for this type of work are found in "Minerals in Rock Sections," by Luquer, D. Van Nostrand Co., and "Characters of Crystals," by A. J. Moses, D. Van Nostrand Co. The preparation and identification of minerals in rock sections, measurement of crystal faces, extinction angles, lines of cleavage, etc., will be excellent, and withal comparatively simple preparation for the study of microsections of rubber. Fred E. Wright (see bibliography) has done some excellent work in the field of the identification of minerals in rocks, through the aid of the petrographic microscope, and any one attempting work in the field of the microscopic examination of rubber compounds will find a careful study of Wright's work to be of great help.

Chapter XII.

Calculation to Approximate Formulas.

The greater number of analyses are made for the purposes of checking factory production, and for comparing finished goods sold under chemical specifications. In such cases, a complete analysis is seldom desired; for factory purposes, a few determinations suffice, and for specification purposes the analysis is carried just far enough to decide whether or not the specifications have been complied with. In the latter case, it is usually sufficient to report the percentage of the rubber present, the presence or absence of reclaimed rubber, the free, total, and barium sulfate-sulfur, the presence and approximate amounts of oils, waxes, mineral rubbers, substitutes, and any other organic fillers likely to have a bearing on the analysis.

There are times when one is interested in learning everything concerning an article, and then, in addition to the foregoing, we need a complete analysis of the mineral fillers, both as to the basic and acidic radicles. From these data, we build up an approximate formula. The report of the analysis should cover the following points:

- Rubber hydrocarbons
- Acetone extract, sulfur free
  - Color and appearance of extract
  - Saponifiable matter
  - Unsaponifiable matter
    - Mineral hydrocarbons
    - Vegetable hydrocarbons
- Chloroform extract
  - Color and appearance of extract
- Alcoholic potash extract
  - Color and appearance of extract
- Total sulfur
- Free sulfur
- Sulfur of Vulcanization

- Glue
- Carbon
- Other organic fillers
- Mineral Fillers
  - Bases
    - Aluminium as Al_2O_3
    - Antimony as Sb_2S_3
    - Barium as BaO
    - Calcium as CaO
    - Iron as Fe_2O_3
    - Lead as PbO
    - Magnesium as MgO
    - Zinc as ZnO
    - Any other bases
  - Acids
    - Carbonate as CO_2
    - Silica as SiO_2
    - Sulfide-sulfur as S
    - Sulfite-sulfur as SO_2
    - Sulfate-sulfur as SO_3
- Organic Accelerators
- Specific Gravity

With these data before us, we may proceed with the reconstruction of the compound.

Rubber. The rubber is the sum of the rubber hydrocarbons (sulfur free), and the acetone, chloroform and alcoholic potash extracts, providing that no organic matter, other than that originally present in the rubber, is shown by the analyses. Ordinarily, with new rubber, the acetone extract will not exceed 4%, the chloroform extract in a properly cured article 2%, and the alcoholic potash extract 1%, based upon the rubber. If any appreciable quantity in excess of these amounts is found, it must be explained.

Sulfur. The sulfur added as such is the sum of the free sulfur and the sulfur of vulcanization, plus any sulfur which may have combined with the fillers during vulcanization. This latter item is often difficult, and sometimes impossible to determine, but a knowledge of the general procedure in designing rubber compounds will be a help.

Organic Fillers. The oils, fats, waxes, etc., are determined

from tests on the acetone, chloroform and alcoholic potash extracts. Mineral rubber at best can be only approximated. Special fillers, such as glue, cellulose, carbon, etc., are set down just as they are determined.

Inorganic Fillers. With a knowledge of what bases and acids are present, we may start to build up the composition of the mineral fillers.

Antimony Compounds. If only antimony, sulfur and calcium sulfate are found, in addition to the rubber, we know that we have a mixture of golden sulfide and rubber, and not only is the calculation simple, but also we have the formula of the golden sulfide used.

Barium. All barium should be calculated to sulfate, unless by analysis barium carbonate is shown to be present.

Calcium. In the absence of antimony, calcium may be calculated to the carbonate, unless the quantity present is less than 1%. In such cases, especially in the absence of reclaimed rubber, it may be assumed, with some assurance, that this small amount was added as hydrated lime. In the presence of whiting, the hydrated lime cannot be detected.

Aluminium. Aluminium is probably present as a silicate. The microscope will be found to be an absolute necessity to determine which silicate is present. In the absence of magnesium a white compound will probably contain aluminum flake, or white clay. Some clays contain titanium, and a positive qualitative test for titanium would be sufficient indication that the substance is clay. Titanium oxide, associated with barium sulfate, is used as a paint pigment, but only in an experimental way in rubber.

Iron. Iron is usually present as the oxide, but frequently is associated with clay. It is sufficient for the purpose to report the oxide and clay separately; then, in rebuilding the compound, any clay in excess of that found in the iron oxide used must be added as such.

Lead. Without question, lead is one of the most difficult substances to work upon. If organic accelerators are present, it is probable that lead oleate, sublimed white or blue lead is present. Probably as safe a thing to do as any is to work up all of the other fillers first, and then apply any sulfide, sulfite, or sulfate-sulfur to the lead.

Magnesia. Magnesia may be present in one of three forms, the

oxide, carbonate, or silicate. With silica present, and no aluminium, a magnesium silicate is probable. In the absence of whiting, any carbon dioxide found is probably combined with magnesium, although lead carbonate (white lead) may interfere. The specific gravity of the compound as a whole is one means for distinguishing between the oxide and carbonate.

Zinc. Zinc is usually present as the oxide, and the simultaneous presence of barytes is not evidence that lithopone is present. In the absence of lead and antimony, any sulfide-sulfur will undoubtedly be combined with zinc. It is best to calculate all zinc as the oxide, and not to assume that lithopone is present unless there is an excess of sulfide-sulfur over that required for lead or antimony.

After the approximate amount of the probable ingredients of the compound have been worked out as above, the sum should be in the neighborhood of 100%—if anything, should exceed that. The next step is to take this formula and calculate the specific gravity, which should check within 0.02 the specific gravity of the original compound. Any greater discrepancy than this reveals some error, which must be checked up. Obviously, if our calculations are low, the high gravity substances are in error, and vice versa. If the gravities agree closely, then the figures may be rounded off to even percentages, to the nearest 0.25%, and brought by adjustment exactly to 100%.

It must be very clear to every one that the interpretation of analytical results is a matter requiring experience, ingenuity, and a great deal of common sense. The intent of the above is certainly not to lay down exact rules, but merely to indicate the general line of thought, permitting the analyst, with his first-hand information as to the progress of the analysis, to make such deductions as may seem wise.

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APPENDIX A.

The Preparation of Materials for Rubber Manufacture.

While to many readers, the factory processes concerned with the preparation of the materials which enter into the composition of a rubber compound are every day affairs, for the benefit of those who are not familiar with the technical processes used in rubber factories, it seems worth while to give some brief description of the various steps. The crude rubber is prepared by washing, if necessary, and by "milling" or "breaking down"; the pigments may be screened or bolted. Certain pigments and organic accelerators are incorporated with rubber to form master batches. These, together with such pigments and crude rubbers as are used in the form in which they are received, are fed to the compound room, where the batches are weighed out according to the prescribed formulas. These batches are mixed in the mill room, and then stored to cool and age. The mixed rubber compound is prepared for manufacturing purposes by (*a*) calendaring into sheets or strips; (*b*) tubing into special or irregular shapes; (*c*) made into a rubber cement by dissolving the rubber compound in benzene, gasoline, or a mixture of the two; (*d*) applied to fabric, either on a calendar, or on a spreading machine. These four classes may be called the "intermediates" of the rubber industry; from these, practically all rubber articles are built.

Washing. The wild rubbers, and the inferior grades of plantation rubber, contain large amounts of bark, dirt, and other foreign matter, and in this condition are not suitable for rubber manufacture. These impurities are removed by washing. The better grades of plantation rubber may be washed in order to be certain that no grit or dirt remains in the rubber, to cause trouble during the service of the articles of which they may form a part.

The washing equipment consists of a vat for heating the rubber, and three washing mills—a cracker, a refiner, and a finisher. Some factories combine the refining and finishing on one mill.

Some of the wild rubbers, notably the fine Para sorts, come in large lumps, or biscuits. Before they are ready for washing, they must be boiled in water for several hours in order to soften them up sufficiently to be worked easily. The large lumps are cut up before being heated.

The cracker consists of two rolls with heavy, coarse corrugations. The rubber is passed through this mill two or three times, just enough to form a thick, rough sheet.

The refiner is a two-roll mill, the front roll having finer corrugations than the cracker. A stream of water plays on the rubber as it passes between the rolls, and as fresh surfaces of the rubber are exposed, the water washes out the impurities.

The finisher is a mill similar to the refiner, but having even smaller corrugations on the front roll. Here the rubber is sheeted out thin, ready for drying.

Drying. Two processes are used for drying: "air-drying" and "vacuum drying."

In the air-drying, the long sheets from the washing mills are hung over poles in a drying room, the temperature of which is maintained at 90-110F.

Fresh air is kept circulating through the room, so as to facilitate drying. In the plantation rubbers, the moisture is usually on the surface only, and such rubbers can be dried in from two to four days. Many of the wild rubbers contain a large amount of moisture, and take up a further quantity during the boiling and washing. This moisture is distributed throughout the rubber, and drying takes from three to five weeks.

In vacuum drying, the rubber is laid on pans, which are placed in a steam-heated vacuum oven. The process requires only a few hours, but it is not particularly well adapted for drying the wild rubbers, since the rapid evaporation tends to form a hard surface film, which hinders further evaporation, prolonging the drying to such a degree as to materially soften and injure the rubber. Soft wild rubbers, such as Guayule, Pontaniak, and the Africans, flow so readily at ordinary temperatures that they cannot be dried on poles, and must be dried in pans, either in the drying rooms or in the vacuum dryers.

Milling, or Breaking Down. Crude rubber varies considerably in quality and in order to lessen the variation, lots of rubber are averaged by the process of "milling" or "breaking down." For this purpose, we use the regular mixing mill, consisting of two smooth rolls, the rear one having a higher circumferential speed than the front one. The rolls are hollow, so as to permit them to be heated, or cooled, in order that they may be maintained at a temperature of about 175F. After the mills have been running a short time, the friction of the rubber is more than sufficient to maintain this temperature, and cold water is kept running through them to prevent them getting so hot as to injure the rubber.

The rubber is fed into the mill, and as it softens it adheres to the front roll. It is cut off, rolled up, and fed back into the mill until it is homogeneous. By this time, it has attained a soft, wax-like consistency. When sufficient uniformity has been attained, the rubber is cut off in the form of sheets, or rolls.

This "milling" not only produces a uniform grade of rubber, but it breaks up the hard, tough particles of crude rubber, and prepares it for the following operations of mixing, calendaring, and tubing.

Master Batches. Some pigments, and many of the organic accelerators, are first mixed with rubber, in what are known as "master batches," before they are sent to the compounding room (where the batches for making the various rubber compounds are weighed out). Pigments such as glue, which requires a longer mixing than can safely be given the entire compound, are first mixed with rubber. Glue, for example, is usually mixed in the proportion of two or three parts of rubber to one of glue. Dusty pigments, such as gas black, are treated in a similar way, frequently in a building separated from the regular mixing room. This step is necessary to prevent the black dust settling down on the other mills, and injuring the colors of the other batches. Organic accelerators are used in small amounts, sometimes 0.2% or less. It is highly important that these small amounts be very evenly distributed throughout the entire compound. After these accelerators have been thoroughly incorporated into a master batch, it is very simple to distribute them throughout a compound. A further advantage is found in the improved accuracy of weighing out the small amounts needed, and elimination of losses of the accelerator during the mixing. Small errors or losses in getting the accelerator into a compound will produce more variation in the finished product than in any other single ingredient.

Screening, or Bolting. Foreign matter, such as wood, grit, pieces of paper or twine from the containers in which the pigments are shipped, are objectionable in many of the better grades of rubber articles. Such impurities are removed from the pigments by sifting the latter through screens of from 40 to 90 mesh, the size depending largely upon the pigment, and the article in which it is to be used.

Compounding. The compounding consists simply in weighing out the proper amounts of pigments and rubbers. These are placed in large iron boxes or pans, and the total weight checked up before leaving the compound room. The usual tolerance in weighing is 0.5 lb. over or under, in a 100 lb. batch, or a total variation of 1%.

Mixing. The mixing mills used for mixing rubber compounds vary from 36 to 84 inches in length, and 20 to 24 inches in diameter. The amount of stock that can be mixed on a mill is largely a function of the width and diameter of the front roll of the mill, and the specific gravity of the stocks; these batches will range from 25 to 225 lbs.

The rubber is first thrown on the mill, together with any pigments put up in master batches,[1] reclaimed rubber, and mineral rubber. After the rubber softens, the pigments and oils are added. Any material which drops between the rolls is caught in a pan, and returned to the rolls until everything has been incorporated. The mixing is continued until the compound is homogeneous, after which it is cut off from the rolls in slabs of about one quarter to three-eighths of an inch in thickness, and weighing 15 to 25 lbs. each. These slabs are laid on racks to cool, after which they are sent to storage bins to age for 24 to 48 hours.

Calendaring. A calendar consists of three smooth hollow steel rolls, accurately ground, arranged vertically, the top and bottom rolls revolving in the opposite direction to the middle roll. The stock, which has been previously softened or "warmed-up" on the regular mixing mill, is fed into the calendar between the top and middle rolls, passes around the middle and under the bottom roll, after which it is wrapped up between cotton liners. The function of these liners is to keep the fresh surfaces of the rubber apart, and protect them from dust and dirt. The thickness of the sheet is controlled by the distance between the top and middle rolls; the width by adjustable knives placed against the rear of the middle rolls. The middle and bottom rolls are further apart than the thickness of the rubber sheet. The bottom roll is cooled, which serves to cool the rubber, and toughen the sheet, before it is wound up in the liner.

The rubber sheet may be made of the desired thickness in one passing through the calendar, or it may be built up from a number of thinner sheets.

Calendaring Rubber to Fabric. When a rubber compound is to be applied to a roll of fabric, the rubber is fed into the calendar as above, and the fabric is fed from the opposite side, between the middle and bottom rolls. The first coat is put on by having the middle roll rotate at a faster speed than the bottom one, giving a grinding action which forces the rubber into the meshes of the fabric. This is called "frictioning." If a further layer of rubber is desired over the friction coat, the rubber and fabric are fed in as before, but the middle and bottom rolls rotate at the same speed, and the sheet of rubber is thus laid on the fabric, and pressed

[1] We have here an added advantage in using organic accelerators in the form of master batches. The accelerator is uniformly distributed throughout the rubber before any of the sulfur is added, thus eliminating largely the danger of partial vulcanization on the mixing mill (called burning, or scorching). It is a well established fact that high concentrations of many of the organic accelerators greatly increase the reaction of vulcanization, especially at the lower temperatures existing on the mixing mill. A compound containing 0.50% of dimethyldithiocarbamate burned in less than one minute after the sulfur has been added, whereas a similar stock, having only 0.05%, mixed without difficulty. Andres (Caoutchouc & Guttapercha *18*, 11089-97 [1921]), showed that 2.5% of thiocarbanilide gave the best cure at 50 minutes, whereas 5% gave a good cure in 3 minutes, and the best cure in 5 minutes. These higher concentrations are easily obtained in a poorly mixed stock, and obviously increase the probability of damage to the stock.

together just sufficiently for them to adhere firmly. This coating of rubber is called the "skim" coat; tire fabric, for example, is usually frictioned on both sides, and skim-coated on one side only. After the skim has been applied the fabric is rolled up between a liner, to be cut up later as desired.

Tubing. The tubing machine is used for irregular strips of rubber, such as tire treads, tire beads, rubber tubing, and the insulation on wire. The essential parts of a tubing machine are a hopper for feeding in the stock, the barrel, which can be heated by steam, and which contains the screw for carrying the stock to the head, and the head, containing the die through which the stock is forced. The head is often heated with a gas jet, to prevent the tubed rubber cooling in the die and coming through rough or cracked. The rubber is warmed up to the desired consistency, cut into small strips, and fed into the hopper. The stock as it comes from the tubing machine is cut in the desired lengths, placed between liners, and set aside to cool.

Cement. In the manufacture of cement, the rubber is warmed up on the mixing mill, and cut off in very thin sheets. A weighed amount of this rubber is cut into small pieces, and thrown into a churn or mixer, to which has already been added the measured amount of solvent. The contents of the mixer are stirred until solution is complete, a matter of from 4 to 12 hours, depending largely upon the nature of the solvent, the grade of rubber, and the efficiency of the mixer. The first mixing usually gives a heavier cement than desired, and this is thinned down with more solvent until the right viscosity is obtained. The nature of the service for which the cement is intended dictates the degree of viscosity.

Spreading. In addition to the method of applying rubber to fabric by calendaring, as described above, we may use the process known as "spreading." A spreader consists of a rubber coated roll, against which rests a heavy knife. Beyond the rubber roll are steam-heated coils or plates, about 18 to 30 feet in length. The rubber compound is first made into a very heavy cement (generally called "dough"). The fabric is passed between the rubber-coated roll and the knife, the dough is applied to the fabric just before the latter reaches the knife, and in passing between the roll and the knife the latter scrapes off all but a thin coating of the cement. As the fabric passes over the heated plates, the solvent in the cement evaporates, and leaves a thin coating of rubber in very intimate contact with the fabric. The space between the knife and roll controls the amount of rubber left upon the fabric. The amount of rubber which may be added at one passing depends upon the ability of the spreader to drive off the solvent during the time when the fabric is passing over the heated rolls. The factors are the temperature and length of the drying plates, and the speed at which the machine is driven. A heavy coating of rubber is obtained by passing the fabric through until the desired quantity of rubber has been applied.

APPENDIX B.

Physical Tests.

The chemist in the rubber factory is usually given the duty of making whatever physical tests may be necessary to determine the properties of the rubber compound or finished article. Similarly, the chemist in the consumer's laboratory supervises and interprets the results of the physical tests made upon samples taken from deliveries of manufactured goods. It seems desirable, therefore, to point out what physical tests are usually made, and their relation to the quality and life of the material.

The principal physical tests are (1) tensile strength, (2) ultimate elongation, (3) set at break, (4) friction. These tests are usually made on the same testing machine. The tensile strength is the force required to break a unit area of a rubber compound; the ultimate elongation is the extent to which the rubber can be stretched before it will break; the set at break is the increase in length of a measured length of rubber, taken at some definite time after break; and the friction is the force required to separate a rubber compound from a piece of fabric to which it has been vulcanized.

Tensile Testing Machine. Three types of machines are in more or less common use in this country: (*a*) Scott; (*b*) Bureau of Standards; (*c*) Schopper.

(*a*) The Scott is a machine of the dead weight type, the pull being against a lever which moves outward as the tension is applied. There are two clamps, into which are inserted the ends of the rubber test pieces. The upper clamp is attached to the end of the weighted lever; the lower clamp is attached to a rod driven at a uniform rate of speed (usually 20 inches per minute for tensile tests, and 2 inches per minute for friction tests). The lever carries a set of pawls, which engage in the teeth of a curved rack, preventing the lever from falling back when the tension is released (as for example, when the test piece breaks). The tension is read off from a dial, the indicator being actuated by the motion of the lever.

(*b*) The Bureau of Standards machine[1] differs from the Scott in that the pull is against a spring balance, which directly records the pull. The clamps are of the same type, and the operation of the machine is essentially the same as that of the Scott.

(*c*) The Schopper machine is one of the dead weight type. The rack, over which the lever moves, is graduated, and the tension is read off opposite the point where the lever stops.

There are a number of styles of clamps which may be used with these machines, the principal ones being the eccentric grip, with its modification consisting of a number of thin disks, mounted eccentrically, the zig-zag grip, which is tightened by a screw, and the spool grips, for use with ring-shaped test pieces. Any of these types may be used with any of the machines mentioned, but the Scott and the Bureau of Standards machines usually carry the eccentric grip clamps, for testing bar-shaped test pieces, whereas the Schopper usually has only the spool grips. As long as the Schopper is equipped only with grips for testing ring-shaped test pieces,

[1] Cf. Bureau of Standards Circular 38, Fourth Edition, p. 53.

it cannot be considered equivalent to the other machines. Between the Scott and the Bureau of Standards machines there is little choice to be made—providing they are both accurately calibrated, and the clamps separated at the same rate of speed, comparable results may be obtained. The dead weight type is usually considered to be the more rugged, and less likely to get out of order, than the spring balance.

When using the ring-shaped test pieces, any one of the three machines may be used without affecting the results. In fact, the type of machine is of importance, not so much for the accuracy of the determinations which it will give, but from the point of view as to how it will stand up under the service given to it, and the convenience of operation.

Shape of Test Pieces. The test piece commonly used in this country for the determination of tensile strength, is the "bar-shaped" or "dumb-bell" test piece. The constricted part is either ¼ or ½" and 1 or 2" long. The ends are enlarged to reduce to the minimum the danger of the test piece tearing in the clamps. The enlarged ends are 1" wide for the ¼" width, and 1¼" wide for the ½" width. A few use a 1¼" width at the ends for a ¼" width at the constricted part, particularly for testing compounds of high rubber content (the so-called pure gum compounds). The style of test piece is largely a matter of the operator's choice, influenced in part by the nature of the material to be tested. Some specifications define exactly the shape, leaving nothing to the discretion of the operator. While theoretically there should be no difference, as a matter of practice results are comparable only when the same shaped test piece is used.

In the above, nothing has been said regarding the thickness of the test piece. Except when slabs are prepared particularly for the purpose of making tensile tests, this is not a matter which can be controlled easily, but the thickness is quite likely to be an important factor, the thicker pieces showing a greater tendency to tear, and hence giving lower results than would be obtained from thinner ones. The most satisfactory practical range is from ⅛ to 3/16" (0.125 to 0.183").

The ring-shaped test piece cannot be compared with the bar-shaped test piece.[2] Its only advantage lies in the fact that with it an autographic chart may be made of the stress-strain curve. With the bar-shaped test piece, to get the same data, it is necessary to use two operators, and from their observations plot the stress-strain curve.

The principal precautions to be taken in preparing test pieces of any shape are that the edges be cut evenly and that the opposite sides of the constricted part are parallel. With ring-shaped test pieces, the rings must be very accurately centered, so as to obtain the same cross-section at all points. If the top and bottom surfaces of the test pieces are not smooth, they should be made so by buffing, so that accurate readings of thickness may be made.[3]

Tensile Strength. The tensile strength is usually expressed in pounds per square inch, or kilograms per square centimeter.[4] The area is usually referred to the cross-section at rest. However, before rubber can be broken, it must be stretched from 300 to 900%, and since there is no change in volume[5] during the stretching, the cross-section at break is very much less than when the test piece is at rest. For this reason, the tensile

[2] This point is argued very convincingly in the Bureau of Standards Circular 38, Fourth Edition, p. 66, etc.

[3] A buffing machine, suitable for the purpose, is described in Bureau of Standards Circular No. 38, Fourth Edition, p. 48.

[4] To convert lbs. / sq. in. into kg. / sq. cm., multiply by 0.07031; to convert kg. / sq. cm. to lbs. / sq. in., multiply by 14.222.

[5] Schippel's change in volume on stretching refers only to the vacua formed around coarse particles of pigment. Such changes are negligible for the calculations under discussion.

strength has sometimes been referred to the cross-section at break, called the "tensile product." This figure is obtained by multiplying the tensile strength by the elongation at break.

The tensile strength is appreciably affected by a considerable number of factors, some of which are within the control of the operator and some are not. Of these, the most important are: rate of separation of the jaws, temperature, size and shape of the test pieces, the direction of the cut (i.e., whether along the length of a calendared sheet, or across), previous stretching of the rubber, and the age of the rubber compound. These factors have been discussed at some length by Whitby,[6] and the Bureau of Standards,[7] and their conclusions may be briefly summarized as follows:

Rate of Separation of the Jaws. The higher the speed, the higher will be the results for tensile strength and ultimate elongation. The range in speeds between 5" and 45" per minute may affect the results anywhere from 5% to 20%. The speed generally employed is 20" per minute.

Temperature. The temperature at which tests are usually expected to be made is 70F. Increasing the temperature lowers the tensile strength and increases the elongation; lowering the temperature produces a reverse effect. It is worthy of notice that for the range of temperature from 50F to 90F, the tensile at break is much more constant than either the tensile strength or ultimate elongation.

Size and Shape of the Test Pieces. There is a tendency for narrow test pieces to develop higher values than wider ones; between ¼" and ½", differences as high as 20% have been noted. Unpublished data may contain instances of even greater variation.

Direction of Cutting. The Bureau of Standards found that the tests made on samples cut in the direction of calendaring show a higher tensile and lower elongation than those cut in the transverse direction. Some experimenters have not been able to duplicate these results, but most of the data on the subject indicate that there is a decided difference between the two directions in a calendared sheet. The ring-shaped test pieces include rubber cut in all directions, and since the break occurs in the direction of least resistance, it is obvious that the effects of calendaring cannot be detected with such test pieces.

Previous Stretching of the Rubber Test Pieces. It is curious that while Memmler and Schob, and the Bureau of Standards, agree that previous stretching alters the results of tensile tests, the former obtained lower results from test pieces subjected to previous stretching, whereas the latter obtained higher figures. Memmler and Schob tested ring-shaped test pieces by subjecting them to 50% of their normal breaking load for a period of 30 minutes, and testing them after a rest period of 24 hours. The Bureau of Standards employed bar-shaped test pieces, stretching to 200%, releasing, and then continuing with an increase of 100% until failure ensued. With high grade material, Memmler and Schob found differences of about 35% loss in tensile strength; the Bureau of Standards found increases of about 20%. Apparently what is needed to determine the exact difference caused by previous stretching, is to combine the two sets of ideas. The Bureau of Standards figures seem to show that short periods of stretching increase the tensile strength. By increasing the time of stressing the test pieces, we could find out whether or not there is a point at which there is no further increase in tensile properties. Similar experiments could be made with ring-shaped test pieces, for it is not at all impossible that the differences may be largely attributed to the differences in the shape of the test pieces.

The greatest importance of these experiments lies in the fact that they

[6] Whitby, Plantation rubber and the testing of rubber.

[7] Bureau of Standards Circular 38, Fourth Edition.

emphasize the necessity for permitting rubber samples to age for at least 48 hours, in order to be certain that they have reached equilibrium.

Aging of the Rubber. Practically every one who has followed the testing of rubber is agreed that a certain time is required after vulcanization for the rubber to come to equilibrium. To be absolutely safe, many have placed the period for aging at 3 days; others think that as little as 24 hours will suffice. In view of the results obtained in a study of the effects of previous stretching, 24 hours seems hardly enough to be on the safe side, and consequently a minimum of 48 hours is recommended.[5]

Ultimate Elongation. The ultimate elongation has been defined as being the extent to which a rubber compound may be extended before rupture will occur. With bar test pieces, the elongation is determined by placing on the constricted portion of the test piece, parallel lines either 1″ or 2″ apart, and then stretching until it breaks. The distance between the marks at break (*a*) less the original distance (*b*) is the elongation (*c*), and is expressed in percentage. Some prefer to express the ultimate elongation by dividing *a* by *b*, giving figures which are 100% higher than the more commonly accepted figures. There is nothing gained by this procedure, and it causes a great deal of confusion when making comparisons. In order to avoid this, many specifications are now being written calling for an elongation in definite figures, such as from 1-5 inches, or 6 inches, or whatever length may be desired.

For correctly cured soft vulcanized rubber, the ultimate elongation is affected most by the amount and grade of rubber present. Compounds containing 90% of rubber will have an elongation of about 900% to 1000%, while compounds containing only 30% will have an elongation of only 300% to 500%. Just as in the case of tensile strength, we find that the ultimate elongation is a more or less arbitrary figure, the value of which will depend to a considerable degree upon the manner of its determination. Practically all of the factors which influence the values for tensile strength will be found to have an effect on those for elongation.

Stress-Strain Curves. If the tensile strength for each increment of elongation be determined. and plotted, the line drawn through these points gives us what is known as the "stress-strain" curve. Generally the strains are plotted as ordinates, and the stresses as abscissæ. The Scott and Schopper machines plot these curves autographically when ring-shaped test pieces are used. With bar test pieces, one operator reads the strains, and the other the stresses. By plotting the curves of a series of cures on one sheet, the effect of time of vulcanization, or whatever other factor it is desired to follow, may be easily observed.

The principal trouble with the stress-strain curve for rubber, is that in making the curves of a series of cures, the first half or three-fourths of the curves take practically the same course, and it is difficult, if not impossible, to notice any appreciable difference until the last quarter of the curve. The Goodyear laboratory has suggested a means for plotting the results in such a fashion as to bring out differences in the early parts of the curves. They plot stresses as ordinates, and the time of cure as abscissæ; for each time of cure, they plot the tensile strength for 100% and each succeeding 100% elongation up to the break. Curves are drawn through all points having the same elongation, and the final curve is drawn

[5] It is obvious that at times these precautions must yield to expediency, and it is frequently more important in manufacturing work to get immediate results which are approximately accurate, than to wait 48 or even 24 hours. We have frequently taken slabs of rubber out of a mold, cooled them in running water for 15 minutes, and then proceeded with the tests. In all such cases, the probability of large errors being present was known and appreciated. Those samples which showed any promise of being satisfactory were given the regular tests 48 hours later, and the latter figures only were used for record and comparison.

through the points of ultimate elongation. The latter is the usual "tensile-strength-time-of-cure" curve used so much by investigators in this country. This system of plotting gives a much more satisfactory picture than does the ordinary stress-strain curve.

Set at Break. After the test piece has been broken on the testing machine it is laid aside for a period which ranges from 1 to 24 hours, according to the methods adopted by the various laboratories, and the increase in the distance between the marks is measured, and calculated to percentage. The set at break for various cures of the same compound passes through a maximum at the optimum cure, the shape of the curve as plotted against time of cure very much resembles the tensile strength-time-of-cure curve. Very little practical use is made of this determination.

A far more extensive use of the determination of set has been made by determining the set on test pieces which have been stretched to less than their ultimate elongation. The usual routine in such tests is to stretch the test piece for ten minutes[9] and measure the increase in elongation ten minutes after releasing. With such tests, there is a drop in the value of the set from an undercure to an overcure, the effect being most noticeable in the former.

Friction. The adhesion between fabric and rubber is termed "friction." There are two methods for its determination: (*a*) the amount of separation under definite load; (*b*) the load required to separate rubber and fabric at a definite rate.

The first method is much employed in testing mechanical goods. In testing belting, for example, a test piece is cut one inch wide and about six inches long. Two plies of fabric are separated; the end of one ply is mounted in a rigid position, while to the other ply is attached a weighted clamp. A mark is made where the test is to start, and the weighted clamp is then released. After a fixed time (generally 10 minutes), the amount of separation is measured. This test merely gives a minimum value, and does not measure the true adhesion.

In the second method, one ply is fastened to the upper clamp of a testing machine, and the other ply to the lower one. The clamps are now separated at a uniform rate, usually 2" per minute, and an autographic record made of the pull required to separate the two plies. This method not only shows the maximum strength of the adhesion, but gives the variation over the area tested, thus revealing any lack of uniformity.

Ordinarily, the adhesion between two rubber plies cannot be tested in this manner, since the joint is usually stronger than either of the two compounds. However, the second method is available for testing adhesions such as are found in the acid cured splice of an inner tube, or between a hard rubber and a soft rubber compound.

Heat Aging Tests. All of the tests described above are performed on test pieces in the condition as they come from the vulcanizers. Such tests give little, if any, idea of what the physical properties of the compound will be at some future time. Artificial means for aging have been suggested, but probably the most widely used is the one developed by W. C. Geer.[10] The test pieces are maintained at a constant temperature of 70C, and tests made at regular intervals until deterioration sets in. The most serious fault with this method is that the heating takes place in air, so that in addition to the deterioration caused by heating, we have the effect of the oxygen of the air. In a great many cases, such as tire frictions, breaker stocks, cushion stocks, etc., heat is undoubtedly the principal agency in deterioration. In such cases, the heating should be done in an

[9] Cf. Bureau of Standards Circular 38, Fourth Edition, pages 57-8, for a description of a convenient form of apparatus for making these tests.

[10] W. C. Geer, India Rubber World 55, 127-30 (1916): W. C. Geer and W. W. Evans, India Rubber World 64, 887-92 (1921).

atmosphere of gas free from oxygen, or any gas which may have a tendency to react with rubber.

The most which can be claimed for this test is that it is useful in comparing compounds of about the same type, or of cures of the same compound. With oxygen excluded, it might be extended to include compounds of different types, which are likely to be exposed to the same degree of heat. Beyond this, we have not succeeded in developing anything reliable in the way of accelerated aging.

APPENDIX C.

TABLE OF SPECIFIC GRAVITIES.

	Minimum	Maximum
Acetone		0.797
Aluminium silicate	2.61	3.02
Aluminum flake	2.56	2.65
Ammonium carbonate	1.50	1.60
Aniline	1.00	1.03
Antimony, red	2.87	
" golden	2.57	2.90
" crimson	3.11	4.20
" black	4.80	
Arsenic yellow	2.75	
Asbestine	2.60	2.82
Asphalt	0.99	
" liquid	0.99	
" Trinidad	1.20	
Balata	1.05	
Barytes (blanc fixe)	4.20	4.92
Beeswax	0.97	
Benzene	0.745	
Bitumen	1.07	1.16
Black substitute	1.10	
Bone black	2.20	2.32
Brown substitute	1.07	1.32
Burgundy pitch	1.10	
Camphene	0.865	
Candelilla wax	0.99	
Carbon bisulfide	1.26	1.29
Carbon black	1.68	1.89
Carbon tetrachloride	1.61	
Carnauba wax	0.995	
Castor oil	0.958	
Ceresin	0.918	0.922
Chloroform	1.52	
Chrome yellow, light	6.41	
" " medium	5.73	5.84
" " deep	5.91	6.08
Chrome green	5.24	5.44
Clay, China	2.60	
" Blue Ridge	2.55	
" Dixie	2.58	
Coal tar	1.05	1.27
Cork	0.24	1.00
Cork dust	1.16	
Corn oil	0.926	0.930
Cotton	1.45	1.55
Cottonseed oil	0.922	0.93
Dimethylaniline	0.958	

	Minimum	Maximum
Diphenylamine	1.16	
Fossil flour	2.00	2.60
Fuller's earth	1.80	2.70
Gasoline, 72-75 Be	0.700	0.707
Glass, powdered	2.49	
Glue	1.30	
Glycerin	1.25	1.30
Graphite	1.95	2.40
Guttapercha	0.96	1.00
Hexamethylenetetramine	1.25	
Indian red	4.80	5.25
Infusorial earth	1.66	1.95
Kaolin	2.75	
Lampblack	1.53	1.75
Lead, chromate	5.65	6.12
" oleate	1.50	
" red	8.17	
" sublimed blue	6.40	
" " white	6.20	6.30
" white	6.10	6.75
Leather fiber	1.40	
Lime	2.21	2.40
Linseed oil	0.94	
Litharge	8.90	9.52
Lithopone	3.60	4.25
Magnesia	2.16	3.65
Magnesium carbonate, light	1.74	2.22
" " heavy	3.00	3.07
" oxide	3.20	
Mica	2.80	3.20
Mineral rubber	1.00	1.06
Montan wax	1.04	
Ochre	3.50	
Ozocerite	0.90	0.95
Palm oil	0.94	
Paraffin	0.869	0.91
" oil	0.90	
" wax	0.91	
Petrolatum	0.90	
Pine tar	1.05	
Pitch	1.23	1.28
Prussian blue	1.96	
Red oxide	4.82	5.16
Rosin	1.05	1.08
Rosin oil	0.98	1.10
Rubber, Accra flake	1.02	
" Amber crepe	0.92	
" Assam	0.967	
" Benguella	0.928	
" Borneo	0.916	
" Cameroon	0.929	
" Cameta	0.916	
" Caucho ball	0.915	
" Centrals	0.93	
" Congo	0.93	
" Guayule	0.975	
" " extracted	0.995	
" Madagascar	0.915	

	Minimum	Maximum
Rubber, Manicoba	0.93	
" Mozambique	0.939	
" Niger flake	0.93	
" Para, coarse	0.95	
" " fine	0.94	
" Penang	0.918	
" Pontianak	0.99	
" Roll brown crepe	0.95	
" Senegal	0.929	
" Sernamby	0.918	
" Sierra Leone	0.923	
" Singapore	0.937	
" Smoked sheets	0.91	0.95
" West Indies	0.935	
Starch	1.50	
Sulfur	1.96	2.07
Sulfur chloride	1.69	1.17
Talc	2.00	2.78
Thiocarbanilide	1.30	
Tripoli	1.95	2.25
Ultramarine	2.30	2.40
Vaseline	0.84	0.945
Venetian red	1.96	2.07
Vermilion	7.89	8.10
Wax tailings	1.00	1.08
White substitute	1.04	1.14
Whiting	2.60	2.72
Wood pulp	1.43	1.46
Yellow ochre	3.50	5.00
Zinc, carbonate	4.42	4.45
" oxide	5.38	5.60
" " leaded	5.64	
" sulfate	3.62	
" sulfide	3.50	

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